

Combined Nanometer-Scale Surface Modification Strategies for the Electrochemical Passivation of Chemically Heterogeneous Aluminum Alloys

Dissertation

Submitted by

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Ich, Tim Hendrik Prüßner, geboren am 19.09.1992 in Herford, bestätige hiermit eidesstattlich als Autor, dass die Ihnen vorliegende Dissertation mit dem Titel „Combined Nanometer-Scale Surface Modification Strategies for the Electrochemical Passivation of Chemically Heterogeneous Aluminum Alloys“, unter der Betreuung von Herrn Prof. Dr.- Ing. Guido Grundmeier, von mir eigenständig angefertigt worden ist. Die verwendeten Quellen und Hilfsmittel sind an entsprechender Stelle genannt, gekennzeichnet und vorschriftsmäßig zitiert. Ich bestätige zudem, dass diese Thesis keiner anderen Prüfungsbehörde in dieser oder ähnlicher Anfertigung vorliegt.

Tim Hendrik Prüßner

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List of publications

Included publications in this thesis:

- 1) **T. Prüßner**, K.-P. Hoyer, N. Buitkamp, P. Vieth, G. Grundmeier, *Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting*, Materials Chemistry and Physics, Volume 349, Part 1, 2026, 131758, ISSN 0254-0584, <https://doi.org/10.1016/j.matchemphys.2025.131758>.
- 2) **T. Prüßner**, K.-P. Hoyer, N. Buitkamp, and G. Grundmeier, *Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting*, Materials and Corrosion (2026): 1-17. <https://doi.org/10.1002/maco.70163>.

Other publications:

- 3) **T. Prüßner**, D. Meinderink, S. Zhu, A. G. Orive, C. Kielar, M. Huck, H.-G. Steinrück, A. Keller, G. Grundmeier, *Molecular Adhesion of a Pilus-Derived Peptide Involved in Pseudomonas aeruginosa Biofilm Formation on Non-Polar ZnO-Surfaces*, Chem. Eur. J. 2024, 30, e202302464. <https://doi.org/10.1002/chem.202302464>
- 4) L. Ruhm, J. Löseke, P. Vieth, **T. Prüßner**, G. Grundmeier, *Adhesion promotion and corrosion resistance of mixed phosphonic acid monolayers on AA 2024*, Applied Surface Science, Volume 670, 2024, 160655, ISSN 0169-4332, <https://doi.org/10.1016/j.apsusc.2024.160655>.
- 5) C. Theile-Rasche, F. Wang, **T. Prüßner**, M. Huck, H.-G. Steinrück, T. de los Arcos, G. Grundmeier, *Evaluation of anti-adhesive and corrosion protection properties of TiAlSiN-magnetron-sputtered films for applications in polymer processing*, Thin Solid Films, Volume 820, 2025, 140676, ISSN 0040-6090, <https://doi.org/10.1016/j.tsf.2025.140676>.
- 6) J. Su, M. Muhle, N. Nembot, **T. Prüßner**, X. Xie, G. Wittstock, G. Grundmeier, *Spontaneous grafting of nitrobenzenediazonium salt on plasma-modified copper substrates*, Electrochimica Acta, Volume 546, 2026, 147810, ISSN 0013-4686, <https://doi.org/10.1016/j.electacta.2025.147810>.
- 7) P. Thissen, G. Wildermann, N. Buitkamp, **T. Prüßner**, G. Grundmeier, *Inhibition of Hydrogen Evolution of Hot-Dip Galvanized Steel in Alkaline Pore Solution by hydrothermally grown ZnO-films*, Materials and Corrosion, under Review

Summary

Aluminum and its alloys are among the most important structural materials in modern lightweight engineering. Their broad range of applications, good processability, and favorable strength-to-weight ratio make them key materials for technologies closely linked to resource efficiency, sustainability, and energy conservation. In addition to conventional manufacturing routes such as casting and wrought processing, additive manufacturing has emerged as a promising production technology in recent years. This approach enables the layer-by-layer fabrication of geometrically complex components based on digital design data and results in characteristic, highly heterogeneous microstructures.

Regardless of the manufacturing route, aluminum alloys commonly exhibit chemically and microstructurally complex surfaces that are governed by the presence of intermetallic phases (IMPs)). These phases not only strongly influence the mechanical properties of the material but also play a decisive role in determining its electrochemical and corrosion behavior. For the long-term durability of aluminum-based materials, it is therefore essential to control the electrochemical activity of such heterogeneous surfaces in a targeted manner. A potential approach is the modification of surface physicochemical properties through molecular adsorption and polymer-based grafting strategies.

From a fundamental perspective, this strategy raises the question of whether chemically heterogeneous aluminum surfaces can be homogeneously and efficiently passivated by a single surface modification strategy, or whether complementary molecular, polymeric, and inorganic thin-film concepts are required to address distinct chemical domains. This question constitutes the central research topic of the present dissertation and is addressed through systematic investigations of selected aluminum alloys in combination with tailored nanometer-scale film systems.

The experimental work focuses on two technologically highly relevant but microstructurally distinct aluminum alloys: an additively manufactured AlSi10Mg alloy and a conventionally produced AW2024 wrought alloy. Owing to their pronounced chemical and electrochemical heterogeneity, both materials are particularly well suited for studying the interplay between alloy microstructure and nanoscale surface coatings.

The first two parts of this dissertation address an additively manufactured AlSi10Mg alloy. The first part focuses on the material in its as-built condition, i.e. directly after fabrication. Investigating this state is of particular relevance for industrial applications, as the economic viability of additively manufactured components depends on their use with little to no post-processing. The study is therefore primarily motivated by technical and application-oriented considerations. The alloy, produced by laser powder bed fusion (LPBF)), exhibits a rough and chemically inhomogeneous surface, as revealed by field-emission scanning electron microscopy (FE-SEM)), energy-dispersive X-ray spectroscopy (EDS)), and digital microscopy (DM)). These characteristics can complicate the direct attachment of molecular or polymer-based thin-film systems. As an initial passivation approach, polydimethylsiloxane (PDMS) is employed. Due to its low surface tension, PDMS can wet the rough alloy surface and can be immobilized on the oxide-covered substrate by UV-induced grafting. Successful PDMS attachment is confirmed by polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS)), X-ray photoelectron spectroscopy (XPS)), and water contact angle measurements (WCA). However, electrochemical impedance spectroscopy (EIS) reveals only a moderate improvement in the electrochemical barrier response. Based on these findings, it is hypothesized that PDMS provides surface coverage

on the micro-/macroscopic scale, while nanoscale electrochemically active sites or transport pathways remain accessible.

Subsequent adsorption of octadecylphosphonic acid (ODPA) onto the PDMS-pretreated surface leads to a pronounced reduction in the electrochemical activity of the AlSi10Mg alloy. The adsorption process is monitored *ex situ* using PM-IRRAS, XPS, WCA measurements, and EIS. In addition, ODPA adsorption on PDMS-grafted surfaces is investigated using two model substrates, namely a polished Al1050 alloy (Al > 99.5 wt%) and a polished silicon wafer, in order to assess the substrate-dependent adsorption behavior of PDMS and ODPA. Based on the collected data, a mechanistic model is proposed in which ODPA adsorption induces a reorganization of the PDMS-modified interphase. This reorganization is interpreted as a preferential interaction of ODPA with accessible Al-oxide-rich surface sites, while PDMS-derived species are assumed to remain more stable on Si-rich or SiO_x-rich surface domains.

The second part of the dissertation builds directly on the findings of the as-built AlSi10Mg study. While the first study demonstrated that PDMS can be introduced onto the rough AM surface, it also revealed limitations with respect to electrochemical barrier performance and suggested a substrate-dependent stability of the PDMS-derived interphase, with Si-rich or SiO_x-rich domains appearing more favorable for PDMS attachment. Therefore, the second study addresses whether a more controlled surface state and a defined SiO_x-based interlayer can improve the formation and functional performance of PDMS-based thin-film architectures. For this purpose, the AlSi10Mg alloy is mechanically and chemically pretreated by grinding, polishing, and chemical etching. After pretreatment, the alloy exhibits a pronounced microstructure composed of a dendritic aluminum matrix surrounded by an eutectic Al-Si phase. Atomic force microscopy (AFM) and scanning Kelvin probe force microscopy (SKPFM) measurements reveal a higher relative Volta potential of the eutectic phase compared with the aluminum matrix, indicating local differences in surface electronic properties that may promote microgalvanic interactions at phase boundaries under corrosive conditions. Linear sweep voltammetry (LSV) and Tafel analysis further confirm increased cathodic reaction kinetics on the unmodified Reference surface. In this context, PDMS is attached either directly to the pretreated alloy surface or to an intermediate SiO_x layer deposited by chemical vapor deposition (CVD). The combined SiO_x-CVD+PDMS modification combines complementary contributions of both individual layers: the SiO_x-CVD interlayer improves the electrochemical response in short-term electrolyte measurements, whereas the PDMS top layer reduces wettability and suppresses electrolyte access under atmospheric conditions. Accordingly, the combined coating architecture shows the most robust overall performance, particularly in chronoamperometry and simulated marine atmospheric corrosion tests.

The third part of the dissertation investigates the adsorption of ODPA and octadecanethiol (ODT) on a T3-tempered AW2024 wrought alloy. This alloy contains a variety of chemically and electrochemically distinct intermetallic particles, many of which are Cu-rich and can strongly influence localized corrosion processes. Particular attention is given to the Al₂Cu phase, which typically acts as a local cathode relative to the aluminum matrix and is frequently associated with pitting corrosion initiation. The molecular strategy in this part of the work is based on combining the affinity of sulfur-containing thiol groups toward Cu-rich surface regions with the strong affinity of phosphonic acid groups toward oxidized aluminum surfaces. In this way, ODT and ODPA are investigated as complementary adsorbates for addressing chemically distinct domains of the heterogeneous AW2024 surface.

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To assess possible selective adsorption on Cu-rich phases, a model Al–Cu alloy containing 5.9 wt.% Cu was additionally used. This model system contains Al₂Cu-like precipitates embedded in an aluminum matrix and enables a more differentiated phase-related analysis than the technically more complex AW2024 surface. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were therefore performed on the AlCu5.9 model alloy to evaluate the hypothesis that ODPA- and ODT-derived species interact differently with Al-rich and Cu-containing surface domains. The results indicate that ODPA-derived species are detected on both investigated microstructural regions, whereas ODT-derived species show a pronounced localization tendency toward Cu-rich phases. The molecular treatments were subsequently transferred to AW2024 in order to assess their effect on the overall surface properties and electrochemical interfacial response of the technical alloy. Dynamic water contact angle measurements and PM-IRRAS analysis show that ODPA-containing treatments produce strongly hydrophobic surfaces with spectroscopic features consistent with alkyl-chain-containing molecular species, whereas ODT treatment alone causes a more moderate change in wettability and a less pronounced spectroscopic signature. Electrochemical investigations using EIS and LSV further show that the interfacial response of AW2024 in chloride-free electrolyte depends on the applied molecular adsorption strategy, with the combined ODPA+ODT treatment showing the highest charge-transfer resistance under the applied conditions.

Overall, the results demonstrate that the performance of nanometer-scale molecular, polymeric, and inorganic thin-film systems is strongly governed by the local chemistry and microstructure of the underlying aluminum alloy. Single-component surface modifications can improve specific aspects of the electrochemical response, but they are often limited when applied to chemically heterogeneous alloy surfaces. In contrast, complementary thin-film architectures that combine different interfacial functions, such as molecular adsorption, polymer grafting, and inorganic interlayers, provide a more effective strategy for addressing distinct surface domains and improving corrosion-related performance under application-relevant conditions.

Zusammenfassung

Aluminium und seine Legierungen gehören zu den wichtigsten Konstruktionswerkstoffen im modernen Leichtbau. Ihr breites Anwendungsspektrum, ihre gute Verarbeitbarkeit und ihr günstiges Verhältnis von Festigkeit zu Gewicht machen sie zu Schlüsselmaterialien für Technologien, die eng mit Ressourceneffizienz, Nachhaltigkeit und Energieeinsparung verbunden sind. Neben konventionellen Herstellungsrouten wie Guss- und Knetprozessen hat sich in den vergangenen Jahren die additive Fertigung als vielversprechende Produktionstechnologie etabliert. Dieses Verfahren ermöglicht die schichtweise Herstellung geometrisch komplexer Bauteile auf Grundlage digitaler Designdaten und führt zu charakteristischen, stark heterogenen Mikrostrukturen.

Unabhängig von der Herstellungsrouten weisen Aluminiumlegierungen häufig chemisch und mikrostrukturell komplexe Oberflächen auf, die durch das Vorhandensein intermetallischer Phasen geprägt sind. Diese Phasen beeinflussen nicht nur maßgeblich die mechanischen Eigenschaften des Werkstoffs, sondern spielen auch eine entscheidende Rolle für dessen elektrochemisches und korrosives Verhalten. Für die langfristige Beständigkeit aluminiumbasierter Werkstoffe ist es daher essenziell, die elektrochemische Aktivität solcher heterogenen Oberflächen gezielt zu kontrollieren. Ein vielversprechender Ansatz besteht in der Modifikation oberflächenphysikochemischer Eigenschaften durch molekulare Adsorption und polymerbasierte Grafting-Strategien.

Aus grundlegender Sicht wirft diese Strategie die Frage auf, ob chemisch heterogene Aluminiumoberflächen durch eine einzelne Oberflächenmodifikationsstrategie homogen und effizient passiviert werden können oder ob komplementäre molekulare, polymere und anorganische Dünnschichtkonzepte erforderlich sind, um unterschiedliche chemische Oberflächendomänen gezielt zu adressieren. Diese Fragestellung bildet das zentrale Forschungsthema der vorliegenden Dissertation und wird durch systematische Untersuchungen ausgewählter Aluminiumlegierungen in Kombination mit maßgeschneiderten nanometerskaligen Filmsystemen bearbeitet.

Die experimentellen Arbeiten konzentrieren sich auf zwei technologisch hochrelevante, jedoch mikrostrukturell unterschiedliche Aluminiumlegierungen: eine additiv gefertigte AlSi10Mg-Legierung und eine konventionell hergestellte AW2024-Knetlegierung. Aufgrund ihrer ausgeprägten chemischen und elektrochemischen Heterogenität eignen sich beide Materialien besonders gut, um das Zusammenspiel zwischen Legierungsmikrostruktur und nanoskaligen Oberflächenbeschichtungen zu untersuchen.

Die ersten beiden Teile dieser Dissertation behandeln eine additiv gefertigte AlSi10Mg-Legierung. Der erste Teil fokussiert sich auf das Material im „as-built“ Zustand, also direkt nach der Fertigung. Die Untersuchung dieses Zustands ist insbesondere für industrielle Anwendungen relevant, da die wirtschaftliche Nutzung additiv gefertigter Bauteile davon abhängt, diese mit möglichst geringer oder ohne Nachbearbeitung einsetzen zu können. Die Studie ist daher vor allem technisch und anwendungsorientiert motiviert. Die mittels Laser Powder Bed Fusion (LPBF) hergestellte Legierung weist eine raue und chemisch inhomogene Oberfläche auf, wie durch Feldemissions-Rasterelektronenmikroskopie (FE-SEM), energiedispersive Röntgenspektroskopie (EDS) und digitale Mikroskopie (DM) gezeigt wird. Diese Eigenschaften können die direkte Anbindung molekularer oder polymerbasierter Dünnschichtsysteme erschweren. Als initialer Passivierungsansatz wird Polydimethylsiloxan (PDMS) eingesetzt. Aufgrund seiner geringen Oberflächenspannung kann PDMS die raue Legierungsoberfläche benetzen und durch UV-

induziertes Grafting auf dem oxidbedeckten Substrat immobilisiert werden. Die erfolgreiche Anbindung von PDMS wird durch Polarisationsmodulations-Infrarot-Reflexions-Absorptionsspektroskopie (PM-IRRAS), Röntgenphotoelektronenspektroskopie (XPS) und Wasserkontaktwinkelmessungen (WCA) bestätigt. Elektrochemische Impedanzspektroskopie (EIS) zeigt jedoch nur eine moderate Verbesserung der elektrochemischen Barrierewirkung. Auf Grundlage dieser Befunde wird die Hypothese aufgestellt, dass PDMS die Oberfläche auf mikro- bzw. makroskopischer Ebene bedeckt, während nanoskalige elektrochemisch aktive Bereiche oder Transportpfade weiterhin zugänglich bleiben.

Die anschließende Adsorption von Octadecylphosphonsäure (ODPA) auf der PDMS-vorbehandelten Oberfläche führt zu einer deutlichen Verringerung der elektrochemischen Aktivität der AlSi10Mg-Legierung. Der Adsorptionsprozess wird ex situ mittels PM-IRRAS, XPS, WCA-Messungen und EIS verfolgt. Zusätzlich wird die ODPA-Adsorption auf PDMS-gegrafteten Oberflächen anhand zweier Modellsubstrate untersucht, nämlich einer polierten Al1050-Legierung und eines polierten Siliziumwafers, um das substratabhängige Adsorptionsverhalten von PDMS und ODPA zu bewerten. Auf Basis der gesammelten Daten wird ein mechanistisches Modell vorgeschlagen, in dem die ODPA-Adsorption eine Reorganisation der PDMS-modifizierten Interphase induziert. Diese Reorganisation wird als bevorzugte Wechselwirkung von ODPA mit zugänglichen Al-oxidreichen Oberflächenbereichen interpretiert, während PDMS-abgeleitete Spezies bevorzugt auf Si-reichen oder SiO_x-reichen Oberflächendomänen stabilisiert bleiben.

Der zweite Teil der Dissertation baut direkt auf den Ergebnissen der as-built AlSi10Mg-Studie auf. Während die erste Studie zeigte, dass PDMS auf die raue AM-Oberfläche aufgebracht werden kann, wurden gleichzeitig Einschränkungen hinsichtlich der elektrochemischen Barrierewirkung sowie eine substratabhängige Stabilität der PDMS-abgeleiteten Interphase deutlich, wobei Si-reiche oder SiO_x-reiche Domänen eine günstigere Anbindung von PDMS nahelegen. Daher untersucht die zweite Studie, ob ein kontrollierterer Oberflächenzustand und eine definierte SiO_x-basierte Zwischenschicht die Ausbildung und funktionelle Leistungsfähigkeit PDMS-basierter Dünnschichtarchitekturen verbessern können. Hierzu wird die AlSi10Mg-Legierung mechanisch und chemisch durch Schleifen, Polieren und chemisches Ätzen vorbehandelt. Nach der Vorbehandlung weist die Legierung eine ausgeprägte Mikrostruktur auf, die aus einer dendritischen Aluminiummatrix besteht, welche von einer eutektischen Al-Si-Phase umgeben ist. Rasterkraftmikroskopie (AFM) und Raster-Kelvinsondenmikroskopie (SKPFM) zeigen ein höheres relatives Volta-Potential der eutektischen Phase im Vergleich zur Aluminiummatrix. Dies weist auf lokale Unterschiede in den elektronischen Oberflächeneigenschaften hin, die unter korrosiven Bedingungen mikrogalvanische Wechselwirkungen an Phasengrenzen begünstigen können. Lineare Sweep-Voltammetrie (LSV) und Tafel-Analyse bestätigen zudem ein erhöhte kathodische Reaktionskinetik auf der unmodifizierten Reference-Oberfläche. In diesem Zusammenhang wird PDMS entweder direkt auf die vorbehandelte Legierungsoberfläche oder auf eine mittels chemischer Gasphasenabscheidung (CVD) aufgebrachte SiO_x-Zwischenschicht angebunden. Die kombinierte SiO_x-CVD+PDMS-Modifikation vereint komplementäre Beiträge beider Einzelschichten: Die SiO_x-CVD-Zwischenschicht verbessert die elektrochemische Antwort in Kurzzeitmessungen im Elektrolyten, während die PDMS-Deckschicht die Benetzbarkeit verringert und den Elektrolytzugang unter atmosphärischen Bedingungen einschränkt. Dementsprechend zeigt die kombinierte Beschichtungsarchitektur die robusteste Gesamtperformance, insbesondere in chronoamperometrischen Messungen und in simulierten marinen atmosphärischen Korrosionstests.

Der dritte Teil der Dissertation untersucht die Adsorption von ODPa und Octadecanthiol (ODT) auf einer T3-wärmebehandelten AW2024-Knetlegierung. Diese Legierung enthält eine Vielzahl chemisch und elektrochemisch unterschiedlicher intermetallischer Partikel, von denen viele Cu-reich sind und lokale Korrosionsprozesse stark beeinflussen können. Ein besonderer Fokus liegt auf der Al_2Cu -Phase, die typischerweise als lokale Kathode gegenüber der Aluminiummatrix wirkt und häufig mit der Initiierung von Lochfraßkorrosion in Verbindung gebracht wird. Die molekulare Strategie in diesem Teil der Arbeit basiert auf der Kombination der hohen Affinität schwefelhaltiger Thiolgruppen zu Cu-reichen Oberflächenbereichen mit der starken Affinität von Phosphonsäuregruppen zu oxidierten Aluminiumoberflächen. Auf diese Weise werden ODT und ODPa als komplementäre Adsorbate untersucht, um chemisch unterschiedliche Domänen der heterogenen AW2024-Oberfläche gezielt zu adressieren.

Zur Bewertung der Hypothese, dass ODPa- und ODT-basierte Modifikationen unterschiedlich mit Al-reichen und Cu-haltigen Oberflächendomänen interagieren, wurde zusätzlich eine AlCu5.9-Modelllegierung untersucht. Dieses Modellsystem enthält Al_2Cu -artige, Cu-reiche Ausscheidungen, die in eine Aluminiummatrix eingebettet sind, und ermöglicht im Vergleich zur mikrostrukturell komplexeren AW2024-Oberfläche eine differenziertere phasenbezogene Analyse. Die ToF-SIMS-Messungen an der AlCu5.9-Modelllegierung zeigen, dass ODPa-abgeleitete Spezies auf beiden untersuchten mikrostrukturellen Bereichen detektiert werden, während ODT-abgeleitete Spezies eine ausgeprägtere Lokalisierungstendenz an den Cu-reichen Phasen aufweisen. Anschließend wurden die molekularen Behandlungen auf AW2024 übertragen, um ihren Einfluss auf die makroskopischen Oberflächeneigenschaften und die elektrochemische Grenzflächenantwort der technischen Legierung zu bewerten. Dynamische Kontaktwinkelmessungen und PM-IRRAS-Analysen zeigen, dass ODPa-haltige Behandlungen stark hydrophobe Oberflächen mit spektroskopischen Merkmalen alkylkettenhaltiger molekularer Spezies erzeugen, während die reine ODT-Behandlung eine moderatere Änderung der Benetzbarkeit und eine weniger ausgeprägte spektroskopische Signatur hervorruft. Elektrochemische Untersuchungen mittels EIS und LSV zeigen darüber hinaus, dass die Grenzflächenantwort von AW2024 in chloridfreiem Elektrolyten von der angewendeten molekularen Adsorptionsstrategie abhängt, wobei die kombinierte ODPa+ODT-Behandlung unter den gewählten Bedingungen den höchsten Ladungsübertragungswiderstand aufweist. Insgesamt deuten diese Ergebnisse darauf hin, dass kombinierte molekulare Funktionalisierungsstrategien das Grenzflächenverhalten chemisch heterogener Al-Cu-Legierungsoberflächen beeinflussen können. Eine eindeutig phasenselektive Adsorption auf der technischen AW2024-Oberfläche konnte jedoch nicht durch alle eingesetzten analytischen Methoden aufgelöst werden.

Insgesamt zeigen die Ergebnisse, dass die Leistungsfähigkeit nanometerskaliger molekularer, polymerer und anorganischer Dünnschichtsysteme stark durch die lokale Chemie und Mikrostruktur der zugrunde liegenden Aluminiumlegierung bestimmt wird. Einkomponentige Oberflächenmodifikationen können einzelne Aspekte der elektrochemischen Antwort verbessern, sind auf chemisch heterogenen Legierungsoberflächen jedoch häufig limitiert. Komplementäre Dünnschichtarchitekturen, die unterschiedliche Grenzflächenfunktionen wie molekulare Adsorption, Polymer-Anbindung und anorganische Zwischenschichten kombinieren, stellen demgegenüber eine wirksamere Strategie dar, um unterschiedliche Oberflächendomänen gezielt zu adressieren und die korrosionsbezogene Leistungsfähigkeit unter anwendungsnahen Bedingungen zu verbessern.

List of Abbreviations

AdC	Adventitious carbon
AFM	Atomic force microscopy
at%	atomic%
BE	Binding energy
CA	Chronoamperometry
CAH	Contact angle hysteresis
CE	Counter electrode
CVD	Chemical vapor deposition
DM	Digital microscopy
DRH	Deliquescence relative humidity
e.g.	exempli gratia
EC	Electrochemical
EDS	energy-dispersive X-ray spectroscopy, Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
eq.	Equation
ERH	Efflorescence relative humidity
FE-SEM	field-emission scanning electron microscopy
HAZ	Heat-affected zones
HR	High-resolution
i.e.	id est
IMPs	Intermetallic phases
IR	Infrared
IRRAS	Infrared reflection–absorption spectroscopy
LPBF	Laser powder bed fusion
LSV	Linear sweep voltammetry
MDRH	Mutual deliquescence relative humidity
OCP	Open-circuit potential
ODPA	Octadecylphosphonic acid
ODT	Octadecanethiol
PDMS	Polydimethylsiloxane
PEM	Photoelastic modulator
PEO	Plasma electrolytic oxidation
PM-IRRAS	Polarization modulation infrared reflection-absorption spectroscopy
r.h.	Relative humidity
RE	Reference electrode
Ref.	Reference from Literature
ROIs	Regions of interest
RT	Room temperature
SAM	Self-assembled monolayer
SAMs	Self-assembled monolayers
SE	Secondary electrons
SHE	Standard hydrogen electrode
SII	Secondary ion intensity
SKPFM	Scanning Kelvin probe force microscopy
TEOS	Tetraethyl orthosilicate
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
TOW	Time of wetness
UV	Ultra-violet
WCA	Water contact angle measurements

List of Abbreviations

WE.....	<i>Working electrode</i>
XPS.....	<i>X-ray photoelectron spectroscopy</i>
ZROIs.....	<i>z-depth ranges of interest</i>

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1. Introduction

In the context of technological developments associated with the fourth industrial revolution, often summarized under the term “Industry 4.0”, industrial production is facing the challenge of fundamentally rethinking established manufacturing processes and infrastructures.¹ Central aspects of this development include digitalization, decentralization, flexible production, and the increasing integration of sustainability-related requirements into technical design and manufacturing strategies.^{2,3} In this context, sustainability, energy efficiency, and resource conservation are no longer merely abstract objectives, but increasingly represent concrete technical requirements. One important contribution to these goals is the extension of the service life of technical materials and components, since material-related failure mechanisms contribute substantially to resource consumption, energy demand, and overall life-cycle costs. The control of corrosion processes therefore plays a central role in improving the durability and reliability of engineering materials.⁴

Aluminum and its alloys are among the most important structural materials in modern lightweight engineering. Owing to their low density, good mechanical properties, and high recyclability, they play a key role in numerous technical applications.^{5–10} In particular, in the transport, aerospace, energy, and structural engineering sectors, aluminum alloys contribute significantly to weight reduction and thus to improved energy efficiency.¹⁰ At the same time, however, the comparatively limited corrosion resistance of many high-strength aluminum alloys remains a major constraint for their long-term application.^{11–14} Corrosion processes not only cause material degradation, but also strongly affect the reliability, safety, and economic viability of aluminum-containing components.

Traditionally, aluminum alloys are produced as cast or wrought materials, where defined microstructures can be adjusted through controlled alloy compositions and heat treatments.^{15,16} In recent years, additive manufacturing has emerged as a comparatively new manufacturing technology that enables suitable aluminum alloys to be processed layer by layer into complex components based on digital design data.^{17–19} This manufacturing route opens new degrees of freedom in component design and allows functionally integrated structures to be produced.²⁰ However, it is also associated with highly non-equilibrium solidification conditions.¹⁸ As a consequence, additively manufactured aluminum alloys often differ substantially from conventionally produced materials in terms of their chemical, microstructural, and surface-related properties.²¹

Irrespective of the manufacturing route, many aluminum alloys share a pronounced microstructural heterogeneity that is characterized by the presence of intermetallic phases (IMPs). These intermetallic constituents differ from the surrounding aluminum matrix in both chemical composition and electrochemical properties.^{22–24} They play a decisive role in determining the mechanical properties of the material,²⁵ but at the same time act as locally active sites for electrochemical processes. In particular, upon contact with chloride-containing aqueous media, such phases may behave as local cathodes or anodes and thereby promote the initiation and propagation of corrosion damage.^{26–28}

Against this background, targeted control of the surface and corrosion properties of aluminum alloys is of central importance for their long-term technical application. In addition to established approaches such as conversion coatings,^{29–31} anodization,^{32,33} and polymer-based coatings,³⁴

nanometer-scale thin-film surface modifications have been increasingly investigated in recent years.³⁵ These include self-assembled monolayers (SAMs), which bind to metal or metal oxide surfaces through specific functional head groups and thereby allow the surface physicochemistry to be tailored.^{36–39} Such systems offer the advantage of forming molecularly defined ultrathin layers while requiring comparatively small amounts of material. Structurally, SAM-forming molecules typically consist of a surface-active head group, a hydrophobic spacer, and a terminal group.^{40,41} The head group largely determines the surface affinity and selectivity of the molecule and thus defines which surface sites can be addressed. On metal and metal oxide surfaces, alkylphosphonic acids^{42,43} and alkanethiols⁴¹ have been particularly widely investigated with respect to their corrosion-inhibiting properties. Another relevant approach is based on polydimethylsiloxane (PDMS), which can be immobilized on oxide-covered metal surfaces in films of only a few nanometers thickness either through condensation reactions^{44,45} or by UV-induced grafting processes.⁴⁶

These molecular and polymer-based thin-film systems can reduce the surface energy of the substrate after successful adsorption or immobilization and thereby generate water-repellent surface properties. This is particularly relevant for protection against atmospheric corrosion, where wettability, electrolyte retention, and the formation of thin electrolyte films are key factors governing corrosion processes.⁴⁷ However, the advantages of such thin-film systems can only be fully exploited if their effectiveness is maintained under the realistic conditions of technical aluminum surfaces. In particular, the pronounced chemical and microstructural heterogeneity of many aluminum alloys remains an insufficiently addressed challenge, since many molecular functionalization strategies implicitly assume a chemically homogeneous substrate surface.

1.1. Motivation and scientific approach

To systematically address this challenge, established molecular, polymeric, and inorganic thin-film modification strategies reported in the literature are applied to two fundamentally different aluminum alloys. The selected systems are chosen such that their chemical functionalities are expected to interact with the dominant chemical features of the respective alloy microstructures, according to current mechanistic understanding.

Most conventional surface functionalization approaches rely on a single anchoring chemistry and implicitly assume a chemically uniform oxide surface. However, both additively manufactured AlSi10Mg and AW2024 exhibit pronounced chemical heterogeneity at the microscale, arising from silicon-rich networks, intermetallic phases, and spatially varying oxide compositions. Under such conditions, a surface modification strategy based on a single anchoring chemistry may be insufficient to achieve homogeneous and functionally effective surface coverage. Instead, selective adsorption or preferential attachment to specific microstructural domains is expected, while other regions may remain insufficiently protected. These locally less-protected areas may act as electrochemically active sites and compromise long-term corrosion resistance.

In contrast, the deliberate combination of modification strategies with complementary chemical functionalities is hypothesized to enable a more targeted interaction with chemically distinct surface domains. By addressing different regions within the heterogeneous microstructure, sequential or combined functionalization may reduce interfacial discontinuities and promote the formation of a more continuous and functionally robust nanometer-scale interphase. Such an

approach moves beyond conventional single-chemistry concepts and explicitly integrates microstructural complexity into the design of corrosion protection systems.

The effectiveness of this chemically tailored, multifunctional interfacial engineering concept is therefore investigated for two technologically relevant aluminum alloys selected on the basis of their fundamentally different microstructural chemistries. In doing so, this work seeks to bridge the gap between classical surface functionalization strategies developed for idealized aluminum or metal oxide surfaces and the practical requirements imposed by chemically heterogeneous engineering alloys.

1.2. Thesis structure

This dissertation is structured to systematically investigate the relationship between microstructural heterogeneity, chemical surface functionalization, and corrosion behavior of aluminum alloys. The overall organization follows a structure–chemistry–function concept, in which fundamental corrosion mechanisms, alloy-specific microstructural characteristics, interfacial modification strategies, and corrosion-related performance are successively linked.

Following the introduction, Section 2 establishes the theoretical and material-specific framework of this work. It first introduces the fundamental principles of aluminum corrosion, including thermodynamic and kinetic aspects of electrochemical processes, passivity, passive film breakdown, and the role of microgalvanic coupling in heterogeneous alloys. Subsequently, corrosion processes under atmospheric and thin-electrolyte-film conditions are discussed, since these conditions are particularly relevant for the surface modifications investigated in this thesis. The section further summarizes the alloy-specific microstructure–corrosion relationships of additively manufactured AlSi10Mg and AW2024, with emphasis on the influence of Si-rich phases, Cu-rich intermetallic particles, and locally varying oxide chemistries. Molecular adsorption, polymer grafting, and inorganic thin-film concepts are then introduced as the basis for the interfacial modification strategies applied in the experimental part of this work. Finally, the section provides the methodological fundamentals of the surface analytical, microscopic, wettability-based, and electrochemical techniques used throughout the dissertation, thereby establishing the conceptual basis for the interpretation of the experimental results.

Section 3 describes the experimental materials, surface preparation procedures, and analytical methodologies employed throughout the dissertation.

Section 4 presents and discusses the experimental results. The first part, Section 4.1, focuses on the molecular and polymer-based functionalization of as-built additively manufactured AlSi10Mg surfaces. This section evaluates whether the rough and chemically heterogeneous as-built surface can be modified by PDMS grafting and subsequent octadecylphosphonic acid (ODPA) adsorption, and whether a combined modification strategy can improve the electrochemical barrier response compared with a single polymer-based surface chemistry. The discussion combines surface morphology, X-ray photoelectron spectroscopy (XPS), polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS), water contact angle (WCA), electrochemical impedance spectroscopy (EIS), and model-substrate experiments to develop a mechanistic interpretation of PDMS/ODPA interfacial reorganization.

Section 4.2 builds on these findings by investigating PDMS grafting on mechanically and chemically pretreated AlSi10Mg surfaces with and without an additional SiO_x-interlayer deposited by chemical vapor deposition (CVD). The aim is to determine whether a more controlled surface state and a defined silicon oxide-based interlayer can improve the formation, stability, and functional performance of PDMS-based thin-film architectures. The section combines field emission- scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), scanning Kelvin probe force microscopy (SKPFM), PM-IRRAS, WCA, XPS, EIS, linear sweep voltammetry (LSV), chronoamperometry, and simulated atmospheric corrosion testing. In doing so, it differentiates between electrochemical stabilization under short-term electrolyte exposure and wetting-controlled protection under salt-contaminated atmospheric conditions.

Section 4.3 addresses a complementary molecular functionalization strategy on AW2024 using ODPA and octadecanethiol (ODT) as adsorbates with different head-group chemistries. To evaluate the hypothesis that these molecules interact differently with Al-rich and Cu-containing surface domains, an AlCu5.9 model alloy is used for phase-related ToF-SIMS analysis. The molecular treatments are then transferred to AW2024, where dynamic water contact angle measurements and PM-IRRAS are employed to assess changes in macroscopic wettability and molecular surface characteristics. Finally, EIS and LSV measurements are used to evaluate how the individual and combined ODPA/ODT treatments influence the electrochemical interfacial response of the technically relevant alloy.

Section 5 summarizes and critically discusses the overall findings of the dissertation with respect to the central research question. The three experimental parts are compared in terms of how nanometer-scale molecular, polymeric, and inorganic surface modifications interact with the compositional heterogeneity of aluminum alloy surfaces and how these interactions affect the resulting interfacial response. Particular emphasis is placed on the potential and limitations of single-component and complementary thin-film strategies, as well as on the methodological implications of investigating phase-specific adsorption and functionality on chemically heterogeneous engineering alloys. Finally, Section 6 provides an outlook on remaining corrosion-related validation steps, correlative approaches for linking local adsorption with local electrochemical activity, and potential application perspectives for complementary nanometer-scale interfacial strategies.

2. Fundamentals

The corrosion behavior of aluminum alloys is governed by a complex interplay of thermodynamic driving forces, electrochemical kinetics, alloy-specific microstructural features, and environmental boundary conditions. While aluminum is generally regarded as a corrosion-resistant material due to the formation of a thin, self-healing passive oxide film, this inherent protection can be locally compromised by alloying elements, IMPs, and surface heterogeneities. As a consequence, the corrosion performance of aluminum alloys is highly sensitive to both the manufacturing route and the resulting microstructure, particularly under atmospheric or thin electrolyte conditions.

In the context of advanced aluminum alloys, such as additively manufactured AlSi10Mg and conventionally processed high-strength Al–Cu alloys, the relationship between microstructure and corrosion behavior becomes even more pronounced. Rapid solidification, non-equilibrium phase distributions, and spatially heterogeneous microstructures characteristic of additive manufacturing introduce additional complexity, which must be considered when evaluating corrosion mechanisms and protection strategies. A sound understanding of these fundamental aspects is therefore essential for the rational interpretation of experimental corrosion data and for the development of effective surface modification concepts.

Beyond the intrinsic properties of the alloy, corrosion resistance is strongly influenced by surface condition and interfacial chemistry. Molecular adsorption layers, polymeric grafting strategies, and inorganic barrier films represent widely investigated approaches to mitigate corrosion by modifying surface energetics, transport properties, and electrochemical reactivity. The effectiveness of such protective concepts depends not only on their chemical composition and bonding mechanisms, but also on their interaction with the underlying alloy microstructure and the surrounding environment.

This section provides the theoretical and conceptual foundation required for the subsequent experimental investigations presented in this work.

2.1. Corrosion of aluminum alloys

The corrosion behavior of aluminum alloys is governed by fundamental thermodynamic driving forces that define the feasibility of electrochemical reactions, as well as by kinetic and interfacial effects that determine their practical relevance. Beyond intrinsic material properties, corrosion processes are strongly influenced by environmental conditions, surface state, and the presence of protective or inhibitive surface modifications.

In order to establish a coherent framework for understanding these interactions, this section first introduces the thermodynamic and electrochemical principles underlying aluminum corrosion, with particular emphasis on electrode potentials and their dependence on environmental parameters. These fundamentals form the basis for the subsequent discussion of aluminum passivity, passive film stability, and mechanisms of localized corrosion. Finally, the implications of these concepts for corrosion inhibition strategies and for corrosion processes under atmospheric and thin-electrolyte conditions are outlined.

The fundamental concepts discussed in this section are based on established textbook knowledge in the field of corrosion science and aluminum corrosion. In particular, the presentation draws on the comprehensive treatments provided by McCafferty et al.⁴⁸, Revie et al.⁴⁹, and Vargel et al.⁵⁰, whose works form the conceptual backbone for the discussion of thermodynamics, passivity, localized corrosion, and atmospheric effects on aluminum alloys. These sources are complemented by additional literature where necessary to address specific aspects relevant to the present study.

2.1.1. Thermodynamics and kinetics of aluminum corrosion

From a thermodynamic standpoint, corrosion processes are driven by a decrease in Gibbs free energy. For electrochemical reactions, the change in Gibbs free energy ΔG is directly related to the electrode potential E according to

$$\Delta G = -nFE, \quad (2-1)$$

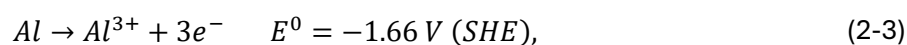
where n is the number of electrons transferred and F is the Faraday constant. This fundamental relationship provides the basis for expressing thermodynamic driving forces in terms of electrode potentials and establishes the link between chemical stability and electrochemical behavior.^{48–50}

Under non-standard conditions, electrode potentials depend on the chemical state of the environment. This dependence is described by the Nernst equation,

$$E = E^0 - \frac{RT}{nF} \ln Q \quad (2-2)$$

where R is the universal gas constant, T the absolute temperature, E^0 is the standard electrode potential and Q the reaction quotient expressed in terms of the activities of the participating species. The Nernst equation highlights that electrode potentials are not intrinsic material constants, but vary with parameters such as ion activity, pH, and temperature. Standard electrode potentials therefore represent reference values corresponding to defined equilibrium conditions and serve primarily as thermodynamic benchmarks rather than predictors of corrosion behavior under practical conditions.^{48–50}

Within this thermodynamic framework, the tendency of aluminum to undergo oxidation can be expressed by the standard electrode reaction



which places aluminum at the extreme active end of the galvanic series.⁵⁰ This highly negative standard potential against the standard hydrogen electrode (SHE) reflects the strong affinity of

aluminum for oxygen and indicates a pronounced thermodynamic driving force for oxidation under equilibrium conditions.

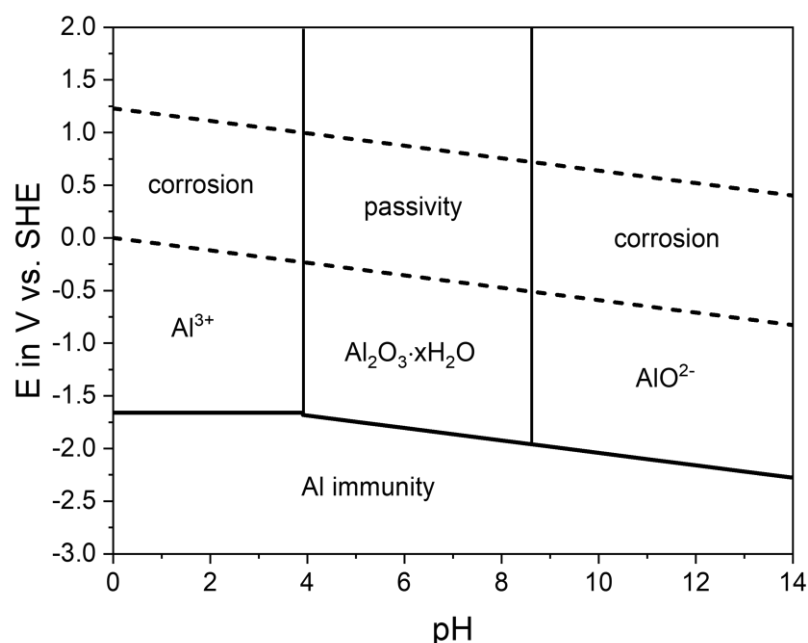


Figure 1. E-pH diagram (also called “Pourbaix-Diagram”) of aluminum in pure water at 25 °C. Adapted from Deltombe and Pourbaix⁵¹.

The pH-dependent stability of aluminum can be further rationalized using the electrochemical potential–pH diagram (also called “Pourbaix diagram”⁵¹) of the Al–H₂O system (see Figure 1). These diagrams are constructed on the basis of thermodynamic equilibria described by the Nernst equation and delineate the stability domains of metallic aluminum, passive oxide or hydroxide phases, and soluble ionic species as a function of electrode potential and pH. For the Al/H₂O system, the Pourbaix diagram indicates that passivity is thermodynamically favored only within a limited pH–potential window, where solid Al₂O₃ or Al(OH)₃ phases are stable. At acidic pH values, aluminum is predicted to dissolve as Al³⁺ species, whereas in alkaline environments dissolution proceeds via the formation of soluble aluminate ions. Consequently, both acidic and alkaline conditions lie outside the thermodynamic stability domain of the passive oxide film.^{48,50}

It should be emphasized that Pourbaix diagrams represent equilibrium conditions based on Nernstian thermodynamics and do not account for kinetic limitations, metastable surface films, or interfacial transport effects. The persistence of passivity on aluminum surfaces under practical conditions therefore reflects kinetic stabilization rather than strict thermodynamic immunity. Nevertheless, Pourbaix diagrams provide an essential conceptual framework for defining the environmental limits of oxide film stability and for interpreting pH- and potential-dependent trends in aluminum corrosion behavior. Properties of the alumina oxide film are further discussed in the following Sections 2.1.2 and 2.1.3.

In real corrosion systems, the measurable electrochemical response is governed by irreversible processes and by the balance between competing anodic and cathodic reactions occurring at the

metal–environment interface. This complex interplay between anodic and cathodic processes was first described by Wagner and Traud in 1938 and is now generally known as the mixed potential theory.⁵² According to this concept, all electrochemical partial reactions contribute to the overall electrochemical activity of a metal surface. This fundamental framework is particularly important for the interpretation of electrochemical measurements on complex metallic substrates under non-ideal and irreversible conditions. Equations. (2-4), (2-5), (2-6) and (2-7) may serve as an illustrative example. Under certain conditions, all cathodic reactions may significantly contribute to the overall cathodic current, whereas the anodic reaction (equation (eq.) (2-3)) generally remains unchanged.⁵⁰

In aerated neutral or alkaline electrolytes, cathodic current is predominantly sustained by oxygen- and H^+ -reduction⁵⁰:



and



Under oxygen-depleted conditions, hydrogen evolution is the main cathodic reaction



In acidic and aerated conditions, the main cathodic reaction can be described as



In irreversible corrosive systems, the open-circuit electrode potential is referred to as the corrosion potential, E_{corr} , and the corresponding current density as the corrosion current density, i_{corr} . Both quantities are linked through the Butler–Volmer equation eq. (2-8), where i denotes the total current density and α_a and α_c the anodic and cathodic symmetry factors

$$i = i_{corr} \cdot \left[\exp\left(\frac{\alpha_a n F (E - E_{corr})}{RT}\right) - \exp\left(-\frac{(1 - \alpha_c) n F (E - E_{corr})}{RT}\right) \right]. \quad (2-8)$$

The potential displacement $E - E_{corr}$ is expressed as the so-called overvoltage η ^{48,49}:

$$\eta = E - E_{corr}. \quad (2-9)$$

To extract kinetic information/parameters from the investigated system by eq. (2-8) the following strategy is usually applied:

Near the E_{corr} , but at sufficiently high overvoltage (usually between ± 60 mV and ± 120 mV)⁴⁸ the so-called Tafel region is established, where either the cathodic or anodic reaction can be neglected. With that in mind, taking the logarithm of eq (2-8) results in the following relations:

$$\log i = \log i_{corr} + \frac{\alpha_a n F \eta}{2.303 \cdot RT} \quad (2-10)$$

and

$$\log i = \log i_{corr} - \frac{\alpha_c n F \eta}{2.303 \cdot RT}. \quad (2-11)$$

The plot of $\log i$ vs. η (or the electrode potential E , also called a “Tafel-plot”) gives a straight line at the Tafel region. With that approach, the Tafel slopes

$$b_a = \frac{d E}{d \log i} = \frac{2.303 \cdot RT}{\alpha_a n F} \quad (2-12)$$

and

$$b_c = \frac{d E}{d \log i} = \frac{2.303 \cdot RT}{-\alpha_c n F} \quad (2-13)$$

can be obtained, as well as the corrosion current i_{corr} . Usually in literature, the value of b_a or b_c are given in $\text{mV} \cdot \text{dec}^{-1}$.^{48,53,54} An example illustrating the graphical application of Tafel analysis to LSV data used in this thesis is shown in Figure 2. The Figure shows, how the kinetic parameters E_{corr} , i_{corr} , b_a and b_c are graphically determined.

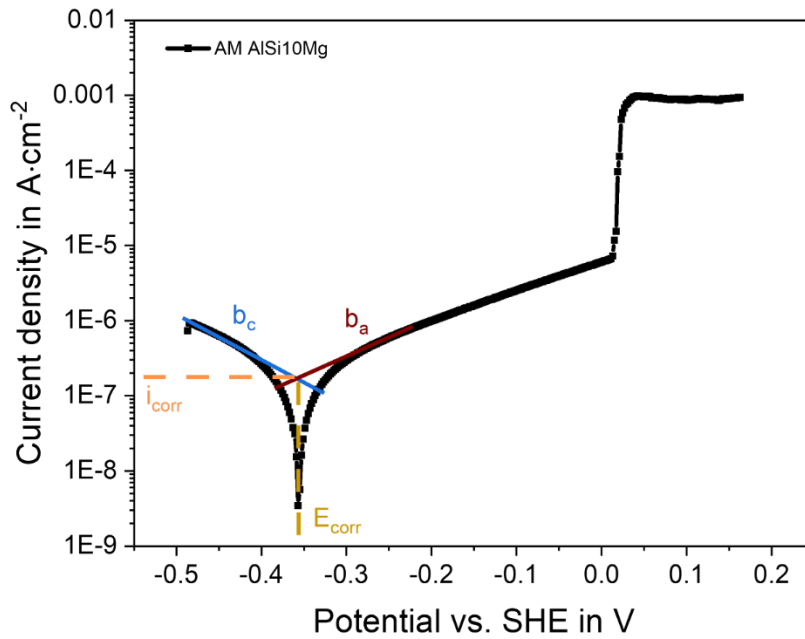
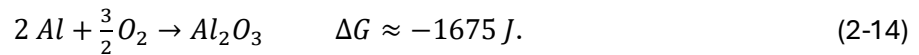


Figure 2. Example of a Tafel evaluation of a representative potentiodynamic polarization curve recorded for a polished and etched AM AlSi10Mg surface in 0.1 M NaCl. The dataset shown was acquired in the course of this thesis.

2.1.2. Passivity of aluminum

The corrosion resistance of aluminum in oxidizing environments is primarily attributed to its ability to form a passive surface oxide film. Upon exposure to oxygen or water, aluminum reacts spontaneously to form a thin oxide layer, which can be described by the reaction



The reaction enthalpy in eq. (2-14) is one of the highest negative of any metal listed in the periodic table.⁵⁰ In ambient environments, the resulting oxide is typically hydrated and may be represented by the general composition $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The oxide film forms within extremely short timescales ($\approx \text{ms}$)⁵⁰ and typically exhibits a thickness of only a few nanometers under ambient conditions.⁴⁸ Despite its limited thickness, the oxide film effectively isolates the underlying metal from the environment and strongly suppresses further metal dissolution.

The protective character of the aluminum oxide film can be rationalized by a combination of thermodynamic, structural, and transport-related factors. Alumina is thermodynamically one of the most stable metal oxides and exhibits a Pilling–Bedworth ratio greater than unity, indicating that the oxide occupies a larger volume than the consumed metal and is therefore capable of forming a continuous, adherent layer.⁵⁰ In addition, the oxide film displays semiconducting properties and acts as an effective barrier to both electronic and ionic transport, thereby limiting the rates of anodic and cathodic reactions at the metal–environment interface.⁵⁵

Structurally, the natural oxide film on aluminum is not homogeneous. It is commonly described as consisting of a compact inner barrier layer directly adjacent to the metal surface and an outer, hydrated amorphous layer that interacts with the surrounding environment. The inner layer provides the primary corrosion protection due to its low defect density and dielectric character, whereas the outer layer is more chemically active and participates in adsorption, hydration, and ion exchange processes. As a result, the oxide film should be regarded as a dynamic interfacial system rather than a static, inert coating.⁵⁵

A defining feature of aluminum passivity is the exceptional ability of the oxide film to reform after mechanical or electrochemical damage. Local disruption of the oxide layer, for example by abrasion or transient electrochemical polarization, is followed by rapid re-passivation on timescales ranging from microseconds to milliseconds.⁵⁰ This self-healing capability ensures that exposure of bare aluminum metal is highly transient and explains why aluminum rarely undergoes uniform corrosion in aqueous environments. Instead, corrosion processes are typically localized and associated with conditions that destabilize the passive film locally.⁵⁶

The stability of the passive oxide film is strongly influenced by environmental parameters, most notably pH and the electrolyte composition. Aluminum exhibits a relatively broad passivity domain in near-neutral aqueous environments, while both acidic and alkaline conditions promote dissolution of the oxide film and reduce corrosion resistance.

For aluminum alloys, passivity is further affected by alloying elements and microstructural features. Alloying elements can segregate to the oxide film, alter its composition, or form mixed oxides with distinct transport and dielectric properties.^{26,57} In multiphase alloys, the passive film may exhibit spatial variations in thickness, composition, and stability, reflecting the underlying microstructure. This has been demonstrated in particular by a combinatorial approach using XPS and ToF-SIMS. Cornette et al. investigated an Al–Cu alloy containing 4.87 wt% Cu in order to determine the surface composition above Al_2Cu particles and the surrounding Al matrix. They first showed that the intermetallic phase present at the surface was confined to Al_2Cu and subsequently performed a detailed XPS and ToF-SIMS analysis. They concluded that the native oxide on the Al matrix (d_{ox}) consists mainly of oxide/hydroxide species with a small amount of Cu(I) oxide and has a thickness of approximately 3 nm. In contrast, the oxide formed on top of the Al_2Cu particles was found to consist of an Al oxide layer of about 2.2 nm (d_{ox}^{I}), followed by copper oxide islands with a thickness of approximately 0.5 nm.⁵⁸ Their model is schematically shown in Figure 3.

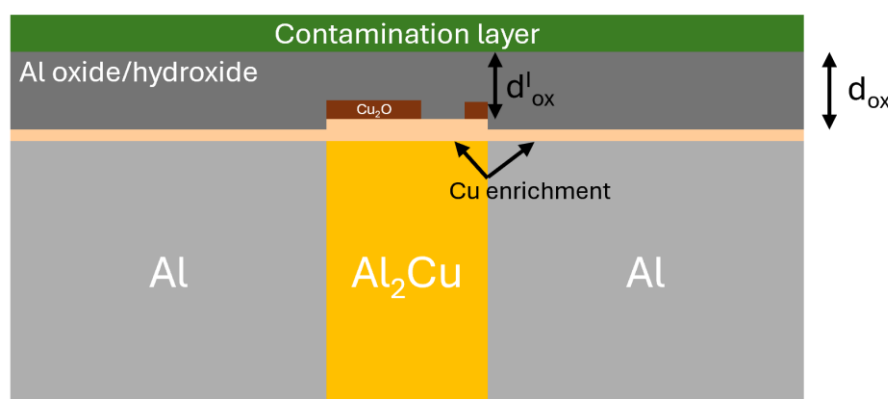


Figure 3. Proposed model of the oxide layer on an AlCu alloy by Cornette et al. The oxide layer thickness d_{ox} account for the oxide thickness on the Al matrix, while d^I_{ox} accounts for the oxide thickness on the Al_2Cu phase. Own illustration, adapted from Ref. ⁵⁸.

Consequently, aluminum passivity must be considered a composition- and microstructure-dependent phenomenon rather than an intrinsic property of pure aluminum.²⁷ This is further discussed in Section 2.1.3.

2.1.3. Passive film breakdown

Although aluminum exhibits remarkable corrosion resistance due to the formation of a thin and stable oxide film, passivity does not represent an absolute or permanent state. Instead, the passive film exists in a dynamic equilibrium between oxide formation and dissolution. Its stability depends sensitively on environmental conditions, electrochemical potential, and the chemical and structural characteristics of the underlying alloy.

Passive film breakdown occurs when this balance is locally disturbed, resulting in the loss of the protective barrier function and the exposure of electrochemically active metal sites. Importantly, breakdown is rarely uniform across the surface. Rather, it is typically a localized process initiated at defects, microstructural heterogeneities, or sites where aggressive species accumulate.⁴⁸ Once initiated, localized dissolution can become self-sustaining under certain conditions, giving rise to phenomena such as pitting corrosion. From potentiodynamic polarization data, the potential at which pitting is assumed to initiate is referred to as the pitting potential, E_p .⁴⁸ Figure 4 shows a typical potentiodynamic polarization curve obtained for AM AlSi10Mg in 0.1 M NaCl, highlighting the position of E_p .

The mechanisms responsible for passive film destabilization can broadly be categorized into environmentally driven effects, such as the presence of aggressive ions, and material-intrinsic factors related to alloy composition and microstructure. Both aspects play a decisive role in determining the susceptibility of aluminum alloys to localized corrosion and are discussed in the following subsections.

2.1.3.1. Chloride-induced passive film breakdown

Chlorides can be found in nearly every natural aqueous system in the world, and it is an essential part of the mammal blood system. However, for almost all metal/metal oxide systems this anion

is known to destabilize passive film causing film breakdown and localized corrosion.^{48,59} Localized corrosion represents a breakdown of passivity that occurs at discrete sites on an otherwise protected metal surface. In contrast to uniform corrosion, where dissolution proceeds relatively evenly across the surface, localized corrosion is characterized by spatial separation of anodic and cathodic regions, with accelerated dissolution confined to small, highly active areas.⁶⁰ Such processes typically involve a sequence of events including passive film breakdown, metastable pit formation, stabilization of localized dissolution, and in some cases re-passivation. The occurrence and stability of localized corrosion are governed by electrochemical conditions, particularly the relationship between corrosion potential, critical pitting potential, and re-passivation potential.^{56,61} For illustration, a typical anodic potentiodynamic polarization curve obtained for an AM AlSi10Mg surface in 0.1 M NaCl is shown in Figure 4. The depicted regions in Figure 4 have to be understood as approximated regions to visualize the theoretical concept. Additionally, it is important to mention, that, in contrast to stainless steel, aluminum has no pronounced active to passive transition at low overvoltages.⁵⁰

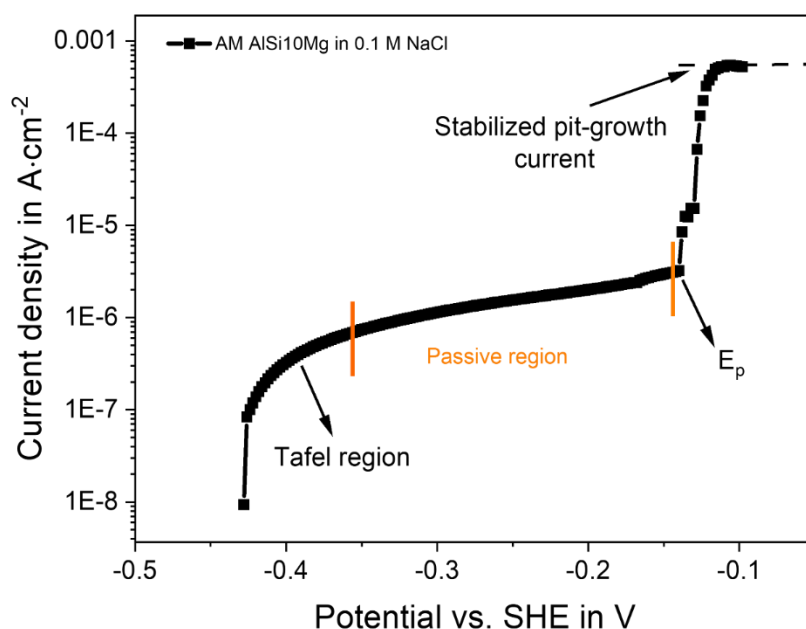


Figure 4. Anodic potentiodynamic polarization curve recorded for a polished and etched AM AlSi10Mg surface in 0.1 M NaCl. The approximate positions of the Tafel region and the passive region are indicated. The passive region is followed by a sudden increase in current density at the pitting potential, E_p , which is attributed to chloride-induced passivity breakdown. At higher potentials, the curve shows a stabilized pit-growth current. The dataset shown was acquired in the course of this thesis.

For aluminum in chloride-containing environments, pitting corrosion constitutes the dominant mechanism of passive film breakdown. The breakdown process does not involve uniform dissolution of the oxide layer but rather a localized destabilization initiated by specific interactions between chloride ions and the passive aluminum oxide film. According to the mechanistic description provided by McCafferty, chloride-induced pitting of aluminum proceeds through a defined sequence of interfacial and transport-controlled steps, visualized in Figure 5 and explained in the following.⁵⁹

The first step involves adsorption of chloride ions onto the hydroxylated aluminum oxide surface. In near-neutral aqueous environments, the native oxide surface carries a net positive charge because the solution pH lies below the isoelectric point of alumina (approximately pH 9–9.5).⁶² Under these conditions, chloride ions are electrostatically attracted to the surface and accumulate at specific sites. Experimental evidence from XPS, X-ray absorption spectroscopy, and radiotracer studies confirm that chloride is adsorbed on the oxide surface prior to pit initiation.^{59,63} Importantly, adsorption is not uniform but preferentially occurs at defect-rich or structurally weak regions of the oxide film.

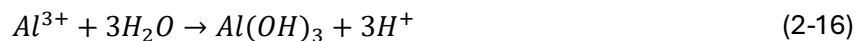
Following adsorption, chloride ions can penetrate the passive film. Two principal mechanisms have been proposed: migration through oxygen vacancies within the oxide lattice and localized film thinning via chloride-assisted dissolution. Analytical studies have demonstrated the presence of chloride not only at the oxide surface but also within the interior of the film, indicating that chloride incorporation precedes macroscopic breakdown.⁵⁹ Notably, complete removal of the oxide layer down to bare metal is unlikely, as freshly exposed aluminum re-oxidizes extremely rapidly. Instead, pit initiation is considered to occur beneath an intact but locally weakened oxide film.⁶⁰

Once chloride ions reach the metal/oxide interface, localized anodic dissolution of aluminum can be initiated. McCafferty describes this process in terms of chloride-assisted electrochemical reactions at discrete sites.⁵⁹ An electrode kinetic model derived in that work predicts a linear dependence of the critical pitting potential on the logarithm of chloride concentration, consistent with experimental observations:

$$E_{pit} = a - b \log [Cl^-] \quad (2-15)$$

where a and b are constants related to reaction kinetics. Within the pH range of approximately 4 to 8.5, the pitting potential is largely independent of pH at constant chloride concentration, underscoring the dominant role of chloride activity in destabilizing the passive state.

Following initiation, pit propagation becomes controlled by chemistry within the occluded corrosion cell. Dissolved Al^{3+} ions undergo hydrolysis according to:



This reaction leads to significant local acidification inside the pit cavity. To maintain electroneutrality, chloride ions migrate into the pit, further increasing local chloride concentration. The combination of low pH and high chloride activity produces a highly aggressive microenvironment that suppresses re-passivation and sustains localized dissolution. Calculations of pit chemistry indicate that the local pH within active pits may decrease to values between approximately 1 and 2.⁵⁹ In addition, hydrogen evolution within occluded regions may generate internal pressure, contributing to blister formation and eventual rupture of the oxide film. The process is schematically shown in Figure 5.

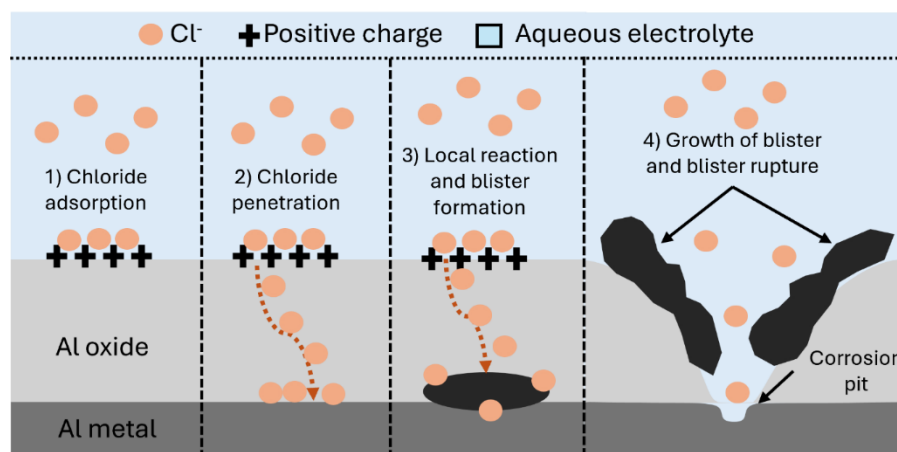


Figure 5. Schematic of proposed chloride-induced localized passive film breakdown and pitting of aluminum. Own illustration, adapted from Ref.⁵⁹.

From a thermodynamic and kinetic perspective, localized corrosion of aluminum occurs only when the applied or the corrosion potential exceeds a critical threshold.⁵⁶ Chloride-induced breakdown should therefore be understood as a potential-dependent electrochemical instability of the passive state, mediated by chloride adsorption, defect-assisted transport through the oxide, localized anodic dissolution at the metal/oxide interface, and the development of an acidic, chloride-enriched occluded environment.

In summary, chloride-induced passive film breakdown on aluminum is a multistep, localized process. It begins with chloride adsorption and incorporation into the oxide, proceeds through defect-mediated penetration and interfacial destabilization, and culminates in the formation of a self-sustaining pit environment characterized by acidification and chloride enrichment. The susceptibility of aluminum alloys to pitting corrosion in chloride-containing electrolytes is therefore governed not only by the inherent stability of the passive film, but by the interplay between chloride concentration, electrochemical potential, and local defect structure within the oxide layer.

2.1.3.2. The role of intermetallic particles and phases

In technical aluminum alloys, the passive oxide film does not form on a chemically homogeneous substrate but rather on a microstructurally complex surface containing intermetallic particles of varying composition, size, and spatial distribution. These phases frequently exhibit electrochemical properties that differ significantly from those of the surrounding aluminum matrix. Therefore, localized breakdown of passivity is often initiated at or in the vicinity of intermetallic particles, making alloy composition and microstructure decisive parameters in corrosion susceptibility.^{48,50}

The fundamental mechanism underlying intermetallic-induced passive film breakdown is microgalvanic coupling. Due to compositional differences, many intermetallic phases possess open circuit potentials that deviate from that of the aluminum matrix. When exposed to an electrolyte, this potential difference leads to the establishment of localized galvanic cells. As summarized in recent analyses of intermetallic corrosion behavior, Cu- and Fe-containing phases such as Al₂Cu, Al₇Cu₂Fe, or Al₃Fe typically act as local cathodes in near-neutral environments,

whereas certain Mg-containing phases (e.g., Mg_2Si or Al_3Mg_2) may initially behave anodically.^{11,57} In Table 1 (Section 2.2.2.2) selected corrosion potentials of the as-mentioned intermetallic particles are listed.

When a cathodic intermetallic particle is embedded within the aluminum matrix, oxygen reduction preferentially occurs on the particle surface. This localized cathodic activity generates hydroxide ions and produces significant alkalization at the particle/electrolyte interface. The resulting increase in local pH can destabilize the passive film on the adjacent aluminum matrix, particularly if the alkalinity exceeds the stability window of $\text{Al}_2\text{O}_3/\text{Al}(\text{OH})_3$ (see Figure 1). Consequently, trenching corrosion frequently develops around cathodic intermetallics, with dissolution confined to the surrounding matrix rather than the particle itself.⁵⁷ In this case, passive film breakdown is indirectly driven by local chemistry changes rather than by direct film penetration. The process is schematically shown in Figure 6.

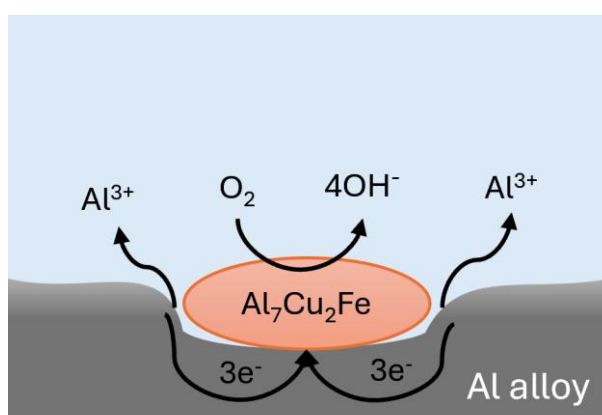


Figure 6. Schematic trenching of a cathodic IMP in an Al-matrix. Own illustration, adapted from Ref.¹¹.

In contrast, certain intermetallic particles may undergo preferential anodic dissolution. Mg-rich particles, for example, often dissolve selectively in chloride-containing or mildly acidic environments. During this process, preferential leaching of Mg can occur, leaving behind a Si- or Cu-enriched remnant. Experimental observations reported by Zhu et al. demonstrate that such dealloyed remnants may subsequently become electrochemically ennobled and behave as cathodic sites.²⁷ This polarity reversal transforms an initially anodic particle into a cathodic center, thereby sustaining continued matrix dissolution. The process is schematically shown in Figure 7. Thus, the electrochemical role of an intermetallic particle is not necessarily fixed but may evolve dynamically during exposure.

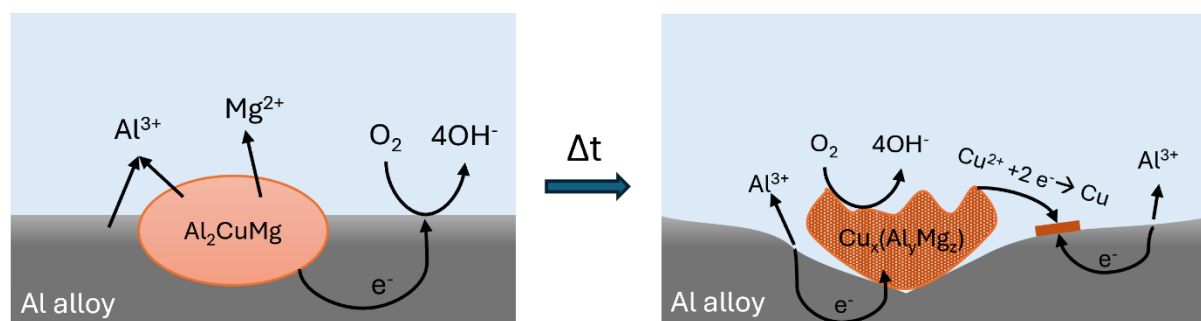


Figure 7. Schematic illustration of anodically induced dealloying of Al_2CuMg IMP. Selective dissolution of less noble constituents results in copper enrichment as a function of time (Δt) and transforms the remaining particle into a cathodically active site. Dissolved copper ions may subsequently be reduced on the surrounding Al matrix, leading to the formation of additional cathodically active sites. Own illustration, adapted from Ref.¹¹.

Microstructural discontinuities at particle–matrix interfaces additionally contribute to passive film instability. Differences in composition, lattice structure, and oxide growth behavior between the matrix and the intermetallic phase can introduce structural defects or thickness variations within the passive layer. Zhu et al. reported that pit initiation frequently occurs at these interfaces, where compositional gradients and oxide inhomogeneities weaken the local barrier properties.²⁷ Such interfacial defects may facilitate aggressive ion ingress or locally enhanced dissolution kinetics.

The severity of intermetallic-induced breakdown is also strongly dependent on particle size and spatial distribution. Larger particles provide greater cathodic area and can sustain higher local current densities, thereby increasing the galvanic driving force.⁴⁸ Clustering of particles may further intensify localized attack by promoting extended galvanic coupling networks. Conversely, very fine and homogeneously distributed intermetallics tend to reduce localized current concentration and may mitigate severe pitting.

Taken together, passive film breakdown induced by intermetallic particles arises from the interplay of microgalvanic coupling, localized pH modification, selective dissolution and dealloying, polarity reversal, and structural discontinuities at phase boundaries. In contrast to chloride-induced breakdown on nominally homogeneous aluminum, this mechanism is intrinsically microstructurally controlled. The passive film is destabilized at chemically and electrochemically distinct heterogeneities, rendering alloy composition and processing history central factors in determining corrosion performance.

2.1.3.3. Interplay of chloride and microstructure-induced passive film breakdown

The mechanisms discussed in Sections 2.1.3.1 and 2.1.3.2 illustrate that passive film breakdown on aluminum alloys can be initiated by both environmental and intrinsic material factors. Chloride-induced breakdown is primarily driven by aggressive anions interacting with and penetrating the passive oxide film. It is fundamentally a chemically and electrochemically mediated instability of the oxide layer, governed by chloride concentration, electrochemical potential, and defect-assisted transport within the film. In this case, breakdown is initiated externally and proceeds via adsorption, incorporation, localized dissolution, and occluded cell chemistry.^{56,59,61,63}

In contrast, passive film breakdown induced by intermetallic particles originates from microstructural heterogeneity within the alloy itself. Here, the destabilization of passivity is not solely dependent on aggressive species but on microgalvanic coupling between phases of differing electrochemical potential. Local cathodic activation, selective dealloying, polarity reversal, and particle–matrix interfacial discontinuities create spatially confined regions where the passive film becomes unstable. This mechanism is therefore intrinsically linked to alloy composition, particle chemistry, and processing history.^{27,57}

In practical systems, both mechanisms are strongly coupled. Chloride ions preferentially accumulate at microstructurally weak or defect-rich sites, such as particle–matrix interfaces. At the same time, galvanic interactions at intermetallic particles enhance local electrochemical activity and facilitate chloride ingress. Consequently, localized corrosion in engineering aluminum alloys rarely arises from a single isolated mechanism but from the combined action of environmental aggressiveness and microstructural heterogeneity.

This interplay underscores that corrosion resistance cannot be fully understood without considering both the stability of the passive film in aggressive electrolytes and the chemical complexity of the underlying alloy. Therefore, alloy composition and microstructure must be explicitly incorporated into any comprehensive assessment of passive film stability. These aspects are addressed in Section 2.2, where the specific microstructural characteristics of the investigated aluminum alloys and individual corrosion protection strategies are discussed in detail.

2.1.4. Atmospheric corrosion of aluminum alloys

While the fundamental electrochemical principles governing aluminum corrosion are well established, their manifestation under atmospheric exposure differs markedly from that in bulk aqueous environments. Atmospheric corrosion occurs under conditions characterized by intermittent wetting, thin electrolyte layers, and continuously changing environmental parameters such as relative humidity, temperature, and airborne contaminants.⁶⁴ As a result, electrochemical processes take place in highly confined and dynamic systems that deviate significantly from classical immersion conditions.

For aluminum and its alloys, atmospheric corrosion represents a particularly relevant exposure scenario, as many applications involve outdoor service or environments where direct immersion is absent. Under these conditions, corrosion behavior is governed by the interaction between the passive oxide film, localized electrochemical activity, and the physicochemical properties of thin electrolyte layers that form on the surface. The limited electrolyte volume, restricted mass transport, and strong coupling to the gas phase fundamentally alter reaction kinetics, interfacial chemistry, and corrosion morphology.

Importantly, atmospheric corrosion does not introduce new corrosion mechanisms, but rather modifies the balance between passivity, passive film breakdown, and repassivation through altered boundary conditions. Phenomena such as oxygen availability, salt deposition, local pH shifts, and microgalvanic interactions become particularly pronounced and can dominate corrosion initiation and propagation. Consequently, understanding atmospheric corrosion requires a framework that integrates the concepts of passivity, electrochemical double layer structure, and microstructural heterogeneity within the context of thin electrolyte layers and transient electrochemical conditions.

The following sections therefore address some key characteristics of atmospheric corrosion of aluminum alloys, with particular emphasis on the properties of thin electrolyte layers, oxygen transport, salt effects, and localized electrochemical processes. These considerations provide the foundation for interpreting corrosion behavior under simulated service conditions and for assessing the effectiveness of corrosion inhibition and surface modification strategies under atmospheric exposure. It should be noted that additional environmental factors influencing atmospheric corrosion, like for example the presence of reactive gases, airborne pollutants, rainfall dynamics, and temperature fluctuations, are not addressed in detail in this section. While these parameters can significantly affect long-term atmospheric degradation, they fall outside the primary scope of the present work. The focus is therefore restricted to those mechanisms that are directly relevant to thin electrolyte layer formation and electrochemical processes under controlled laboratory conditions.

2.1.4.1. Establishment of thin electrolyte layers

Atmospheric corrosion of aluminum alloys is governed by electrochemical processes that occur under conditions fundamentally different from those in bulk aqueous electrolytes. Instead of immersion in a continuous liquid phase, the metal surface is typically covered by thin electrolyte layers that form as a result of humidity-induced condensation, adsorption of water vapor, or deliquescence of deposited salts.⁶⁵ These electrolyte films often exhibit thicknesses ranging from a few nanometers to several micrometers and are spatially and temporally heterogeneous.^{66,67}

The relative humidity (r.h.) is a key parameter for the establishment of thin electrolyte layers in specific environments. It is defined as⁵⁰:

$$r.h. = 100 \cdot \frac{e}{e_w}. \quad (2-17)$$

Essentially, relative humidity is defined as the ratio between the actual water vapour pressure, e , and the saturation vapour pressure, e_w , at a given temperature. In Ref⁵⁰, atmospheric humidity levels are categorized as “dry” (r.h. < 30%), “normal” (r.h. < 80%), “humid” (r.h. > 80%) and “saturated” (r.h. = 100%). Another important parameter in this context is the dew point, i.e. the temperature at which condensation begins. The dew point depends directly on the relative humidity.⁵⁰

In a short digest of Sereda in 1975 it was stated that metals corrode at an accelerated rate when the r.h. exceeds approximately 75 % in outdoor conditions,⁶⁸ which is in good agreement with more recent reports.⁶⁹ This can be attributed to the fact that only limited surface cooling is then required to reach the dew point. The exact temperature difference required for condensation depends on the actual surface environment; however, for a clean surface, Ref.⁵⁰ reports a value of approximately 4–5 °C. Even when the dew point is not reached, water can still adsorb on metal surfaces as a function of relative humidity, making r.h. a critical factor in atmospheric corrosion.⁵⁰ If pollutants such as chlorides or sulfates are also present, corrosion processes may already be initiated under these conditions.

Another important factor influencing the formation of thin electrolyte films on a surface is the hygroscopicity of deposited salts. The hygroscopicity of salts and other compounds determines

their phase transitions, i.e. deliquescence and efflorescence, at different relative humidities and is directly related to the hygroscopic properties of the solute.⁷⁰ The relative humidity at which a salt particle spontaneously adsorbs large amounts of water and transforms into a saturated droplet is referred to as the deliquescence relative humidity (DRH),⁷⁰ and the corresponding solid-to-liquid transition is termed deliquescence. Efflorescence is the reverse transition, i.e. from liquid to solid, and occurs at a relative humidity below the DRH. The relative humidity at which this transition takes place is called the efflorescence relative humidity (ERH).⁷⁰ Both DRH and ERH are compound-specific. For NaCl, the DRH is typically reported between 73% and 77%, whereas the ERH lies between 41% and 51%.⁷⁰ Thus, with regard to atmospheric corrosion, the establishment of thin electrolyte layers is governed not only by the ambient relative humidity, but also by the presence and hygroscopic properties of compounds deposited on the surface.

2.1.4.2. Corrosion kinetics under thin electrolyte films and droplets

The defining characteristic of thin electrolyte layers is their limited volume and restricted mass transport. In contrast to bulk solutions, diffusion of dissolved species within thin films is strongly constrained by the small electrolyte thickness and by lateral confinement. As a result, electrochemical reactions can induce pronounced local gradients in ion concentration, pH, and dissolved oxygen.⁶⁵ These gradients can develop rapidly and persist over extended periods due to the limited ability of the system to equilibrate with the surrounding environment.

Oxygen transport is in fact a key distinction between thin electrolyte layers and bulk electrolytes. In bulk solutions, the overall corrosion rate is often governed by the diffusion of oxygen through the electrolyte, which is typically described in terms of a diffusion-limited cathodic current density. In contrast, due to the small diffusion path length and the proximity to the gas phase, oxygen availability is often enhanced under thin electrolytes.⁷¹ This correlation has been explicitly studied by Cheng et al on AA2024 substrates.⁶⁶ They used an advanced experimental set-up, which ensured precise establishment of thin electrolyte layers coupled with the possibility of making electrochemical measurements. The authors found that cathodic currents increased markedly when the electrolyte layer thickness decreased under 200 μm , which they assumed to be the Nernstian diffusion layer thickness of oxygen. Above 200 μm , cathodic currents were similar to bulk conditions. Interestingly, the cathodic currents slightly decreased between an electrolyte thickness of 50-100 μm , which the authors attribute to corrosion products blocking cathodic sites on the aluminum alloy or hindering oxygen diffusion towards them.⁶⁶ This finding could explain why atmospheric corrosion is found to be not as severe as compared to immersion corrosion for many metals.⁴⁹ Similar approaches have been done by Liao et al.⁷² and Zhong et al.⁷³ who found similar trends of increased cathodic currents under thin electrolyte thicknesses.

The electrochemical behavior of aluminum under thin electrolyte layers is further influenced by the intermittent nature of surface wetting. Atmospheric exposure is typically characterized by repeated wet-dry cycles governed by relative humidity, temperature fluctuations, and the presence of hygroscopic contaminants. During wetting events, electrochemical reactions can proceed, whereas drying leads to concentration of dissolved species, precipitation of salts, and partial interruption of ionic conduction. Such cyclic conditions promote transient electrochemical activity and can repeatedly drive the system across stability thresholds for passivity.⁴⁸ An example of an advanced experimental set-up to evaluate the as-mentioned influence of wet-dry cycles by electrochemical methods has been done by Nishikata et al. in 1997.⁶⁷ The authors developed an experimental set-up in which stainless steel samples are first exposed in chloride containing solution and then allowed to dry in a specified environment.

During that time, the specimens were continuously tracked by AC impedance and corrosion potential tracking methods. The wet-dry process has been performed several times to simulate accurate atmospheric exposure. The authors conclude that pit initiation takes place especially during the dry cycle as the chloride concentration increases.⁶⁷ Similar results have been found by Tsutsumi et al. by the usage of droplet drying.⁷⁴

Another often used approach to simulate atmospheric corrosion is the evaluation of corrosion during or after droplet contact with the metallic surface. Usually, droplets are used to simulate condensation processes taking place on the surface, which are, due to their limited volume, usually also associated with the establishment of thin films.⁷¹ Historically U. R. Evans first used this droplet approach in 1926 to study the corrosion kinetics on metals under droplet exposure. He found that cathodic reactions are located at the edges of the droplet, while anodic reactions are located in the middle of the droplet. As a consequence, cations (both from the electrolyte and the metal) will move towards the cathode to account for charge neutrality, while anions move towards the anode. Corrosion products precipitate between the anodic and cathodic zone.⁷⁵ The conclusions he drew remain valid today and are proven in many publications.^{75,76} The experimental approach and the main findings are schematically summarized in Figure 8.

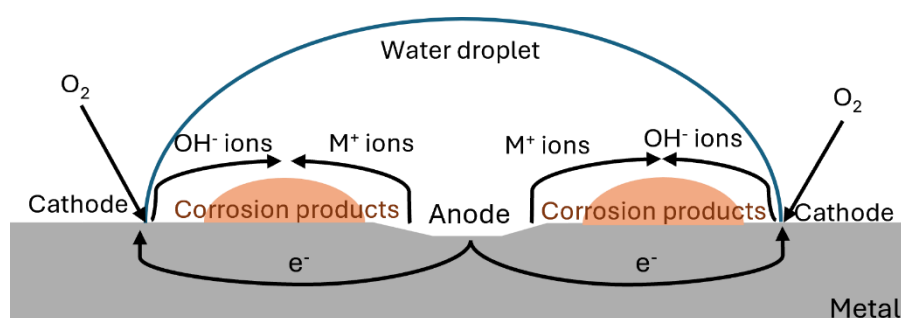


Figure 8. Schematic of general corrosion processes under a droplet of electrolyte. Own illustration, adapted from Ref.⁷¹.

In the review of Koushik et al. from 2021, droplet and their morphology on the atmospheric corrosion is explained as follows: Under droplet electrolytes, atmospheric oxygen only need to traverse a very short diffusion path between the air–electrolyte interface and the metal surface. The geometric curvature of the droplet further influences oxygen transport. The shortest diffusion path exists near the droplet perimeter, leading to spatial variations in oxygen availability across the metal surface. This establishes a differential aeration cell, in which regions near the droplet edge become relatively cathodic compared to the oxygen-depleted central area, thereby driving localized corrosion processes. Changes in droplet size modify the radius of curvature and consequently alter the extent of differential aeration, directly affecting the corrosion mechanism and its localization.⁷¹ The change in droplet size (due to evaporation) can also influence the convection within the droplet so that corrosion products and other electrochemically active species can be distributed over the wetted surface.⁷⁷

Another aspect that must be considered when simulating atmospheric corrosion using droplet corrosion is the dynamics of the droplet volume. The concentration of dissolved salts, which determines the conductivity of the electrolyte, varies as a function of droplet volume.⁷⁴ As corrosion proceeds, the accumulation and dilution of corrosion products within the confined

electrolyte are likewise governed by droplet size. Moreover, droplet dimensions are not static but evolve dynamically in response to environmental factors such as temperature, relative humidity⁷⁴, the presence of hygroscopic salts, atmospheric pollutants, surface wettability, and precipitation of corrosion products⁷⁷. In a study of Tsuru et al. it has been found that droplets can also be surrounded by micro-droplets and wetting films during droplet corrosion.⁷⁸ The authors attributed this phenomena to cathodic alkalization processes and their induction of osmotic processes. Water and cations (e.g. Na^+) move towards the alkalized sites to dilute and account for negative excess charges. It is assumed, that this movement leads to the enrichment of water in the wetting film and to the formation of microdroplets. Interestingly, the formation of microdroplets was cation specific, which the authors attribute to solubility properties.⁷⁸ In another study by Gateman et al. the authors reported a spreading of the electrolyte on cathodic active zones, supporting the findings of Tsuru et al.⁷⁹

The influence of salts and gases on atmospheric corrosion on aluminum under high humidity conditions (r.h. $\approx 95\%$) has been intensively studied by the group around Johansson and Svensson et al.⁶⁴ The authors reported that NaCl is highly corrosive towards aluminum. They also investigated the influence of CO_2 on the corrosion of aluminum. In the absence of CO_2 the aluminum substrates showed high proportion of general corrosion with no to less pitting events, while in the presence of CO_2 less general but more pitting corrosion was observed. The authors interpret these results in the following way: If CO_2 is absence, the surface of aluminum is quickly alkalized due to the basic reaction formulated in eq. (2-4), which accelerates general corrosion. The high pH also hinders the chloride ions from adsorbing due to the negative charge of the surface (see Section 2.1.3.1). If CO_2 is present, the alkalization is reduced by the reaction of CO_2 with OH^- ions to form carbonates. This leads to the adsorption of chlorides which in turn favors pitting corrosion.⁶⁴

Electrolyte composition within thin films differs markedly from that of the original condensed or deposited solution. Evaporation and limited replenishment lead to enrichment of aggressive species, such as chloride ions, and to strong shifts in local pH.⁶⁷ These compositional changes are particularly critical for aluminum, whose passive oxide film exhibits a limited thermodynamic stability window with respect to pH (see Section 2.1.2). Consequently, thin electrolyte layers provide conditions under which passive film stability and breakdown can be strongly decoupled from the chemistry of the bulk environment.

In summary, thin electrolyte layers represent a highly dynamic electrochemical environment characterized by restricted mass transport, evolving chemistry, and intermittent wetting. These conditions fundamentally alter the balance between passivity, passive film breakdown, and re-passivation on aluminum surfaces. Understanding the characteristics of thin electrolyte layers is therefore essential for interpreting atmospheric corrosion phenomena. In the next section common strategies to inhibit atmospheric corrosion on aluminum are presented and discussed.

2.1.4.3. Inhibition strategies for atmospheric aluminum corrosion

As already outlined in Sections 2.1.4.1 and 2.1.4.2, significant differences exist between atmospheric corrosion and immersion corrosion. Although the underlying electrochemical reactions are fundamentally identical, the boundary conditions governing electrolyte formation, transport processes, and mass exchange differ substantially. Consequently, conventional corrosion protection strategies, as described in Sections 2.2.1.3 and 2.2.2.3, can in principle also be applied to atmospheric environments. However, because atmospheric corrosion is controlled

by the intermittent presence of thin electrolyte films rather than bulk solutions, this section focuses specifically on protection concepts that address the unique characteristics of thin electrolyte layers, with particular emphasis on wettability and surface property modification.

In atmospheric environments, corrosion of aluminum alloys requires the formation of a sufficiently conductive electrolyte layer, typically arising from condensation, precipitation, or salt deliquescence. A key parameter controlling this process is the time of wetness (TOW), defined as the duration during which a metal surface remains covered by a liquid film capable of supporting electrochemical reactions.⁴⁷ Corrosion can only proceed when anodic and cathodic sites are electrically connected through an electrolyte. Hence is the reduction of electrolyte contact, continuity, or conductivity of thin electrolyte layers directly limiting corrosion activity. Wetting and drying processes are governed by surface energy, capillary condensation, adsorption phenomena, and environmental humidity fluctuations making interfacial thermodynamics central to atmospheric corrosion control.⁴⁷

In marine and industrial atmospheres, deposited hygroscopic salts such as NaCl play a decisive role in electrolyte formation. When the relative humidity exceeds the DRH, solid salt particles absorb moisture and form concentrated brines.^{47,70} For mixed salt systems, the “mutual deliquescence relative humidity” (MDRH) may be significantly lower than that of the individual salts, thereby extending the environmental window in which liquid films persist.⁴⁷ Even extremely thin electrolyte layers and droplets formed in this manner are capable of sustaining localized corrosion.^{67,80} Their stability depends strongly on interfacial energy balances. The thermodynamic stability of a liquid film on a surface is governed by the relationship between solid–gas, solid–liquid, and gas–liquid surface tensions. These energies are related in the Young-Dupré equation as follows:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{GL} \cdot \cos(\theta), \quad (2-18)$$

where γ_{SG} denotes the surface tension between the solid and gas phase, γ_{SL} between the solid and liquid phase, γ_{GL} between the gas and the liquid phase and θ the contact angle between a liquid drop on a solid.⁴⁷ Equation (2-18) is strictly valid only for flat, smooth and homogeneous surfaces. The Young-Dupré equation is further discussed in the context of surface energies in Section 2.4.4.1.

If the contact angle given in eq. (2-18) diminishes to zero, the liquid spreads over the surface forming a thin wetting film. Spreading is determined by the difference of surface energies between the solid and the wetted solid:

$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{GL}). \quad (2-19)$$

If S is positive ($0^\circ \leq \theta < 90^\circ$), the liquid wets the surface, if S is negative ($\theta > 90^\circ$) the liquid is said not to wet or partially wet the solid.^{47,81} Thus, surface energy directly determines whether condensed water forms a continuous film, discrete droplets, or de-wets entirely. Examples of

water droplets with a positive S value (Figure 9, left) and a negative S value (Figure 9, right) are shown in Figure 9.

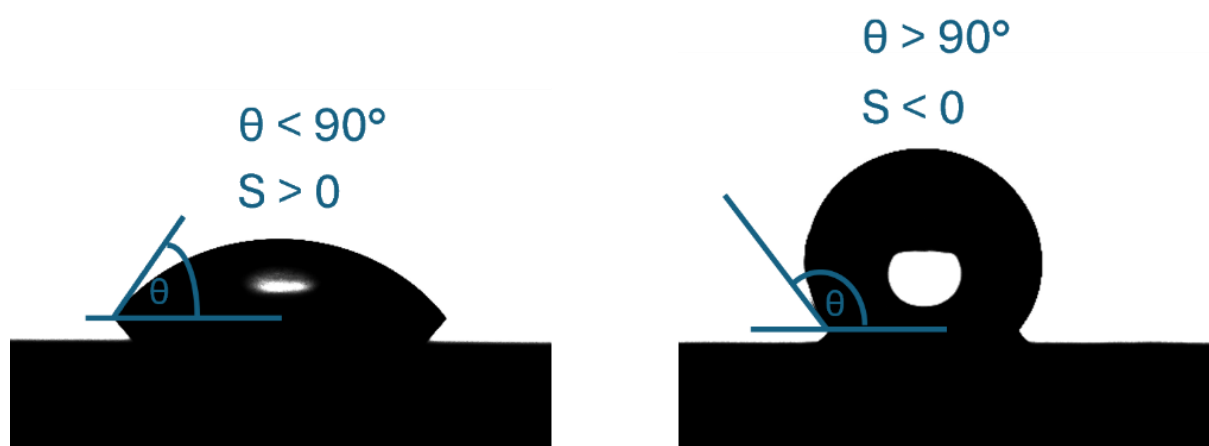


Figure 9. Example of partially wetting (left) and non-wetting surface from metal samples studied in this thesis.

Modification of surface wettability therefore represents a particularly effective strategy for atmospheric corrosion inhibition. By lowering the solid–liquid interfacial energy and increasing the apparent contact angle, hydrophobic and superhydrophobic surfaces reduce the effective contact area between electrolyte and substrate.

A widely applied approach to render metallic surfaces hydrophobic is the spontaneous adsorption of surfactant-like molecules. Molecules exhibiting this behavior are commonly referred to as self-assembled monolayers (SAMs). Typically, such molecules consist of a functional head group that chemisorbs onto the metal surface, a molecular spacer (often an alkyl chain), and a terminal functional group that defines the surface energy and physicochemical properties of the modified interface, as this terminal group forms the new outer surface.^{35–37,39,40,82}

To achieve water repellency, the terminal group frequently consists of nonpolar moieties such as methyl ($-\text{CH}_3$) functionalities. The chemical and physicochemical fundamentals governing SAM formation, structure, and stability are discussed in more detail in Section 2.3.1.

SAM adsorption has been demonstrated on a wide variety of metallic and semiconducting substrates, including Au, Si, Cu, and Al, and can generally be implemented using comparatively simple experimental procedures. The effectiveness of SAM-based surface modification for atmospheric corrosion protection has been verified in several studies, demonstrating their ability to reduce electrolyte adhesion and limit corrosion under thin-film conditions. For example, Hosseinpour et al. have shown in 2013, that alkanethiols can lower the corrosion susceptibility of copper against formic acid containing humid air.⁸³ The authors additionally correlated higher alkane spacer chain length with higher corrosion protection properties, which is supported in many other studies. In a similar approach, Zhao et al. showed that alkylphosphonates (octadecylphosphonic acid, ODPA) can also lower the susceptibility of copper against formic acid containing humid air.⁸⁴ In a study of Maxisch et al. was found that ODPA on aluminum oxide surfaces reduces the amount of adsorbed water in humid air.⁸⁵ However, the authors also found that water was able to penetrate the SAM formation thus indicating possible pathways for

electrolyte to pass through. In a study of Hintze et al. the authors found that the applied organosilane SAM on Al surfaces do increase polarization resistance only for a limited amount of time, contributing to the findings of Maxisch et al. that SAMs can be penetrated by electrolytes.⁸⁶

The fabrication of superhydrophobic surfaces is inspired by the so-called “lotus effect.” The fundamental concept is to first introduce a controlled micro- and nanoscale surface roughness and subsequently apply a low-surface-energy coating, for example based on SAMs.⁸⁷ On superhydrophobic surfaces, water droplets adopt a composite solid–air interface (Cassie–Baxter state), where air pockets trapped within surface microstructures minimize direct liquid–solid interaction.⁸⁸ This configuration provides two primary protective effects. First, the reduced solid–liquid contact area limits ionic transport and slows charge transfer between the electrolyte and the aluminum surface. Second, the low adhesion of droplets facilitates their removal by gravity or minor external perturbations, thereby shortening the time of wetness and removing deposited salts.⁸⁸

Beyond passive water repellency, recent work has demonstrated that superhydrophobic surfaces may exhibit coalescence-induced droplet self-jumping behavior.⁸⁹ During condensation, neighboring microdroplets merge and convert excess surface energy into kinetic energy, causing the merged droplet to spontaneously detach from the surface. This mechanism enables electrolyte removal even in the absence of external forces. Electrochemical impedance spectroscopy measurements have shown that such dynamic droplet removal significantly enhances corrosion resistance under atmospheric exposure.⁸⁹

Despite these advantages, the protective performance of hydrophobic and superhydrophobic surfaces is not unconditional. Under cyclic humidity conditions, salt deliquescence, recrystallization, and capillary infiltration may induce a transition from the Cassie–Baxter state to the Wenzel state, in which the electrolyte penetrates the surface microstructure and increases the solid–liquid contact area.⁸⁹ Such transitions compromise the air barrier effect and may restore conditions favorable for localized corrosion. Furthermore, mechanical degradation, contamination, or chemical aging of low-surface-energy functional groups can increase wettability and prolong electrolyte retention.

In summary, inhibition strategies for atmospheric aluminum corrosion based on wettability modification operate by fundamentally altering interfacial thermodynamics and electrolyte dynamics rather than directly suppressing electrochemical kinetics. By reducing surface energy, limiting electrolyte adhesion, shortening time of wetness, and promoting droplet removal, hydrophobic and superhydrophobic modifications disrupt the conditions necessary for sustained thin-film corrosion. Their effectiveness, however, depends critically on environmental stability and the long-term maintenance of surface structure and chemistry under realistic atmospheric exposure conditions.

2.2. Alloy specific fundamentals and microstructure-corrosion relationships

As has been depicted in the previous section, the corrosion behavior of aluminum alloys is strongly governed by the interplay between alloy composition, microstructure, and processing route. While general electrochemical principles provide a common framework, the manifestation

of corrosion processes is highly alloy-specific and critically dependent on the microstructural and interfacial characteristics introduced during manufacturing.

In the present work, particular emphasis is placed on additively manufactured AlSi10Mg alloys, which constitute the primary material system under investigation. Additive manufacturing processes, such as laser powder bed fusion (LPBF), generate non-equilibrium microstructures characterized by refined cellular networks, solute segregation, and a high density of interfaces. These features result in complex surface chemistries and oxide compositions that differ fundamentally from those of conventionally processed alloys and can significantly influence passive film stability as well as the adsorption and self-assembly of corrosion-inhibiting molecules.

In addition to the additively manufactured alloy, the AW2024 aluminum alloy with T3 tempering is considered as a second, technologically relevant and corrosion-sensitive system. AW2024 is characterized by a heterogeneous distribution of Cu containing intermetallic phases that promote pronounced microgalvanic interactions and localized corrosion. The coexistence of multiple electrochemically distinct phases leads to spatial variations in oxide composition and interfacial chemistry, posing substantial challenges for the design of effective surface modification and coating strategies.

This section therefore addresses the alloy-specific fundamentals and microstructure–corrosion relationships of both material systems, with particular focus on the interfacial characteristics that must be considered for achieving effective and durable corrosion inhibition.

2.2.1. Additive Manufactured AlSi10Mg alloys by LPBF

2.2.1.1. Principle manufacturing process and resulting microstructure

Metal additive manufacturing comprises several processing routes, including powder bed fusion, directed energy deposition, and binder jetting. Among these technologies, LPBF has become the most established method for processing Al–Si casting alloys such as AlSi10Mg due to its high geometrical resolution and stable processability.¹⁷ In the present work, all additively manufactured specimens were produced by LPBF. Accordingly, this section focuses exclusively on this manufacturing route.

In LPBF, thin layers of gas-atomized AlSi10Mg powder (typically 20–60 μm) are spread across a build platform using a recoating mechanism. A focused laser beam selectively scans the powder bed according to the digital cross-section of the component, locally melting the powder particles and forming a transient melt pool. After solidification, the build platform is lowered by one layer thickness, a new powder layer is deposited, and the scanning process is repeated. This layer-by-layer principle enables the fabrication of complex three-dimensional geometries directly from computer-aided design data.⁹⁰ The principle manufacturing approach is schematically shown in Figure 10.

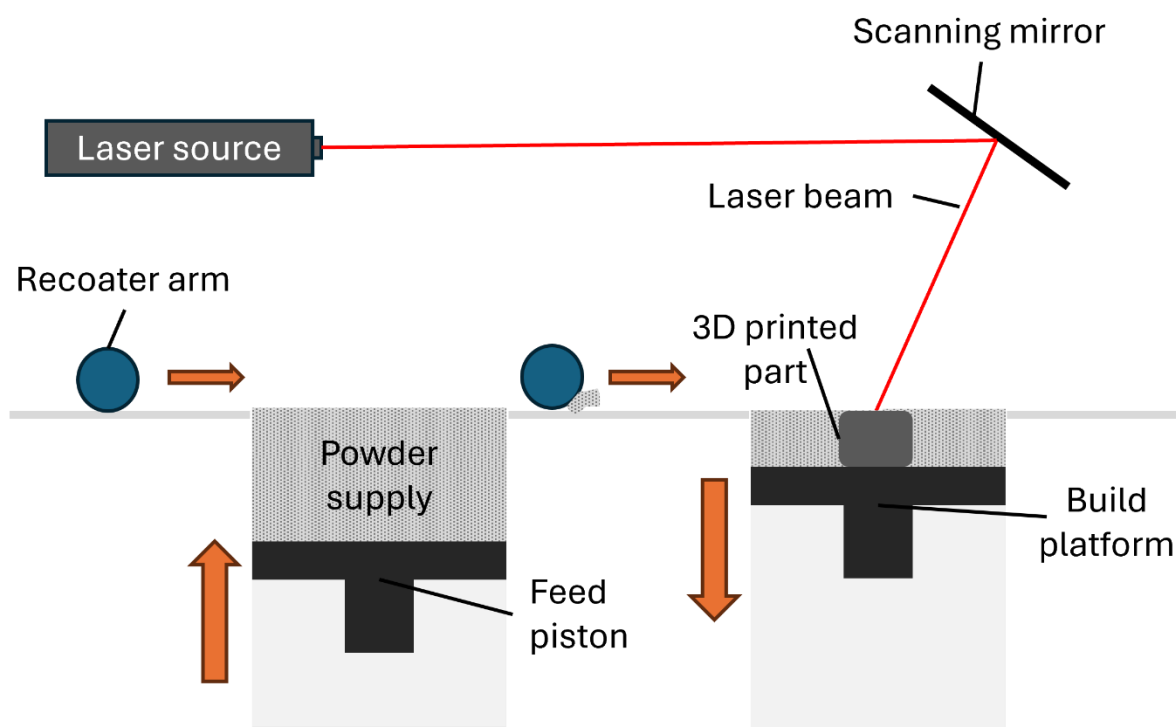


Figure 10. Schematic illustration of the LPBF process. A laser beam is directed onto the powder bed via a movable scanning mirror, melting the first layer of the three-dimensional part. The recoater arm then distributes a new powder layer from the powder supply onto the build platform, while the build platform is lowered by approximately one layer thickness. The laser subsequently melts the newly deposited powder layer. This sequence is repeated until the part is fully built. Own illustration, adapted from Ref.⁹⁰.

The process is conducted under inert gas atmosphere, most commonly high-purity argon. In some systems nitrogen is used; however, argon is generally preferred for aluminum alloys to avoid potential nitride formation. Oxygen levels are typically around a few ppm to minimize oxide growth and ensure stable melt pool dynamics. A controlled gas flow across the build chamber additionally removes process by-products such as metal vapor and spatter.⁹⁰

During laser exposure, powder particles are rapidly heated above the liquidus temperature and fuse with the underlying solidified layer, ensuring metallurgical bonding between successive layers. Due to the small melt pool volume and efficient heat dissipation into the previously solidified material and the build platform, extremely high cooling rates (10^5 – 10^6 K·s⁻¹) and steep thermal gradients occur.⁹¹ Each newly deposited layer partially remelts the top region of the previous one, resulting in repeated thermal cycling and strongly non-equilibrium solidification conditions.^{17,18} These processing conditions lead to a distinct hierarchical microstructure. On the microscale, overlapping melt pools reflect the local thermal history and scan strategy.

Within the melt pools, rapid solidification promotes the formation of a fine cellular α -Al matrix with characteristic cell sizes below 1 μ m. Silicon is rejected during solidification and segregates along the cellular boundaries, forming a continuous Si-rich network. Due to solute trapping under high cooling rates, the α -Al matrix is supersaturated compared to equilibrium conditions.¹⁸ The resulting microstructure is therefore highly refined and contains a large density of internal phase boundaries.

In contrast, conventionally cast AlSi10Mg solidifies under significantly lower cooling rates. The microstructure consists of coarse α -Al dendrites and eutectic silicon in plate-like or fibrous

morphology, depending on modification treatment. The phase distribution is closer to thermodynamic equilibrium, and the density of internal interfaces is markedly lower. Consequently, LPBF processing generates a substantially finer and more interface-dominated microstructure than conventional casting.^{17,18}

These differences are of direct relevance for corrosion behavior. The refined α -Al/Si phase distribution alters microgalvanic coupling conditions, while the high density of phase boundaries and potential differences in oxide formation affect electrochemical heterogeneity at the surface. Therefore, additively manufactured AlSi10Mg represents a fundamentally different corrosion substrate compared to conventionally processed Al–Si alloys, which must be considered when evaluating inhibition and coating strategies.

2.2.1.2. Correlation between microstructure and corrosion behavior

The corrosion behavior of AlSi10Mg is fundamentally governed by its phase distribution and the electrochemical interaction between the α -Al matrix and Si-rich phases. Silicon exhibits a more noble corrosion potential than aluminum and therefore acts cathodically when coupled to the surrounding Al matrix, establishing microgalvanic cells in chloride-containing environments.^{56,92,93} As a consequence, the spatial distribution, morphology, and continuity of the Si phase critically determine the localization and kinetics of corrosion processes.

In LPBF-processed AlSi10Mg, rapid solidification promotes the formation of a fine cellular α -Al microstructure with silicon segregated along submicrometer cell boundaries.^{17,18,94} This morphology results in a high density of α -Al/Si interfaces. Although an increased interface density could theoretically intensify galvanic interactions, several studies report that the extremely fine and homogeneous Si distribution in the as-built LPBF condition often leads to a more uniform corrosion morphology compared to cast or heat-treated conditions.^{92,95–99} The refined Si network distributes cathodic sites more evenly, thereby reducing local current concentration effects and mitigating deep localized attack.

Thermal exposure or post-build heat treatment induces coarsening and spheroidization of the Si phase.^{92,95,97–99} The initially continuous Si network decomposes into larger, more isolated particles. This coarsening enhances the local cathode-to-anode area ratio and increases the effective microgalvanic driving force at discrete sites, thereby promoting pit initiation adjacent to coarse Si particles.^{95,100} Consequently, while heat treatment may improve ductility or relieve residual stresses, it can simultaneously reduce corrosion resistance due to altered galvanic architecture.

^{92,95–99}

Beyond phase morphology, the global corrosion behavior of LPBF AlSi10Mg is influenced by process-induced structural heterogeneity. The layer-wise fabrication strategy generates melt pools, melt pool boundaries, and heat-affected zones (HAZ) with distinct thermal histories.^{92,101,102}

Figure 11 shows scanning electron micrographs of a polished and etched LPBF-manufactured AlSi10Mg surface at different magnifications. The image on the left highlights the HAZ associated with the boundaries of the laser scan tracks. The image on the right displays a magnified region within a single melt track, revealing the characteristic dendritic sub-microstructure of the alloy.

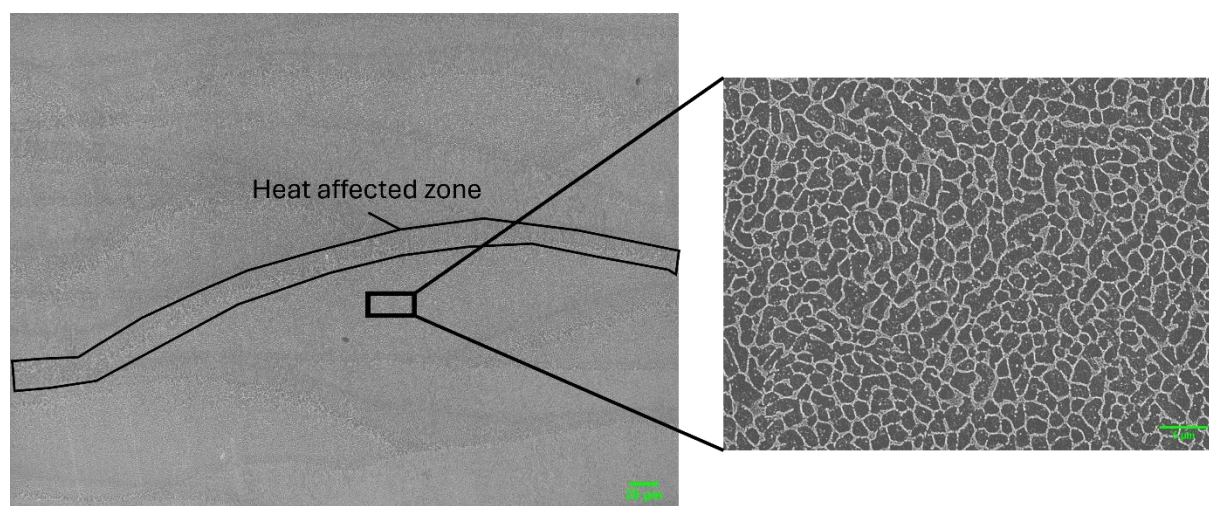


Figure 11. SEM recordings of a typical LPBF-manufactured AlSi10Mg surface after polishing and etching used in this thesis. Indicated is the heat-affected zone (HAZ, left image) and a magnification of the dendritic microstructure (right image).

Melt pool boundaries may exhibit local microsegregation and variations in defect density, which can lead to differences in electrochemical activity relative to the melt pool interior.⁹² Furthermore, repeated thermal cycling during layer deposition affects precipitate evolution and residual stress distribution²⁵, potentially modifying passive film stability.^{92,97} Under corrosive conditions, preferential attack along melt pool contours has been reported, indicating that mesoscale process features contribute to corrosion localization.^{92,101} Therefore, slight differences in corrosion behavior are observed between build orientations, reflecting variations in melt pool boundary structure and microstructural anisotropy. However, these differences seems to be small.^{95,101}

When compared to conventionally cast AlSi10Mg, distinct differences in corrosion behavior become evident. Cast alloys typically contain coarse eutectic Si particles within an α -Al dendritic matrix, resulting in stronger localized galvanic coupling and enhanced pitting susceptibility.^{21,96} However, this advantage of AM processing diminishes after thermal treatment, when the Si morphology approaches that of cast material.^{92,95,97,98}

Overall, the corrosion response of AlSi10Mg is controlled by the interplay between microgalvanic coupling and process-induced structural heterogeneity. In LPBF material, both the fine-scale Si network and the hierarchical melt pool architecture define the electrochemical behavior across multiple length scales. A comprehensive understanding of these microstructural features is therefore essential for interpreting corrosion mechanisms and for designing effective inhibition strategies.

2.2.1.3. Corrosion protection strategies and challenges

As discussed in the previous section, corrosion protection strategies must be tailored to both the structural and chemical heterogeneity of the additively manufactured AlSi10Mg surface in order to achieve maximum efficiency. Since corrosion processes are governed by electrochemical reactions, any effective corrosion protection strategy must be capable of inhibiting these reactions. In the present section, a selected overview of the current state of the literature

regarding corrosion protection strategies for additively manufactured AlSi10Mg alloys is provided, and the associated challenges are briefly discussed.

The first studies considered in this state-of-the-art review address, among other aspects, the corrosion behavior of polished and as-manufactured (i.e., rough) surface conditions of additively manufactured AlSi10Mg. In both investigations, it was concluded that the as-manufactured surfaces exhibit a lower corrosion resistance compared to their polished counterparts. This behavior was primarily attributed to the presence of surface porosity and cavities inherent to the as-built condition, which can act as preferential sites for localized corrosion initiation and promote electrolyte retention.^{101,103}

Furthermore, Cabrini et al. demonstrated that the application of a cerium-based conversion coating on rough as-manufactured surfaces was not effective, as the coating was unable to form a continuous and compact protective film. The pronounced surface roughness and topographical heterogeneity hindered uniform nucleation and growth of the conversion layer, resulting in incomplete coverage and reduced barrier performance.¹⁰¹

Since it is generally advantageous to minimize post-processing steps after component fabrication, particularly with respect to corrosion protection, there is strong interest in coating or surface modification strategies that can be applied directly after manufacturing. Reducing mechanical surface preparation not only lowers processing time and cost, but also preserves the as-built microstructural features that may be functionally relevant. Consequently, corrosion protection approaches that are compatible with the as-manufactured surface condition are of particular importance for additively manufactured aluminum alloys.

A traditional and widely established surface treatment for aluminum alloys is anodization. This electrochemical process promotes the controlled growth of an oxide layer on the aluminum surface, thereby enhancing barrier properties and improving corrosion resistance. Its industrial maturity and scalability make anodization an attractive candidate for integration into post-processing routes of additively manufactured components.¹⁰⁴

This coating/surface modification approach has also been applied to additively manufactured AlSi10Mg substrates, and its beneficial effects on corrosion resistance have been confirmed. In particular, anodization was shown to reduce corrosion current densities and enhance barrier properties through the formation of a protective oxide layer.^{105,106} However, microstructural investigations revealed the presence of defects along Al/Si interfaces within the anodized layer. These regions can act as preferential pathways for electrolyte penetration and may compromise long-term corrosion protection. The heterogeneous distribution of silicon in the AM microstructure appears to influence local oxide growth kinetics, leading to discontinuities or microstructural inhomogeneities in the anodic film.¹⁰⁶ In addition to these interfacial challenges, anodization may adversely affect mechanical properties. The formation of a relatively brittle oxide layer and potential alterations in the near-surface microstructure can reduce fatigue performance or introduce stress concentrations, particularly in components subjected to cyclic loading.¹⁰⁵

A conceptually similar but more energetic oxidation process is plasma electrolytic oxidation (PEO), which extends conventional anodization by operating at higher voltages and inducing localized plasma discharges at the metal–electrolyte interface.¹⁰⁷ During PEO, the substrate is connected as the anode in an electrical circuit, and a continuous direct current (DC) is applied against a cathode (typically steel). The electrolyte system usually consists of an aqueous alkaline solution containing dissolved silicate species (e.g., Na₂SiO₃). The resulting PEO coating thickness typically ranges between 10 and 80 μm and appears, among other factors, to be influenced by the

morphology of the silicon network in the AM microstructure.^{108–110} Across the studies considered in this literature review, significant improvements in corrosion performance were reported. Corrosion current densities were reduced on average by one to two orders of magnitude, while charge transfer resistances (determined by electrochemical impedance spectroscopy, EIS) increased substantially.^{108–110} Notably, all referenced studies indicate that as-manufactured AM AlSi10Mg samples formed the most protective PEO layers compared to heat-treated or as-cast specimens.^{108–110} This suggests that PEO represents a promising corrosion protection strategy for additively manufactured AlSi10Mg alloys.

However, despite these improvements, PEO coatings inherently contain micro-pores and discharge-induced defects that can act as localized pathways for electrolyte penetration.¹¹¹ Long-term corrosion resistance therefore depends strongly on defect density, coating thickness uniformity, and the integrity of the dense inner barrier layer.¹⁰⁹ Consequently, while PEO represents a robust barrier-based strategy, its performance remains closely tied to microstructural compatibility and defect management.

Another relevant corrosion protection strategy is based on sol–gel coatings. In this approach, metal alkoxides undergo hydrolysis and condensation reactions to form polymeric networks. The process proceeds through several stages: first, a colloidal suspension (the “sol”) is formed; this subsequently polymerizes into a three-dimensional network, resulting in a “gel.” In a final step, thermal treatment is typically applied to dry the gel. Depending on the drying conditions, either xerogels or aerogels can be obtained. When applied as coatings, sol–gel films are generally subjected to rapid drying (often referred to as gelation) to form thin protective layers.¹¹²

In a study by Macera et al., such a sol–gel coating strategy was applied to AM AlSi10Mg specimens to improve their corrosion resistance. To evaluate corrosion performance, salt spray testing was conducted. The authors reported significantly enhanced corrosion resistance and good chemical stability of the coating.¹¹³ Nevertheless, challenges remain in achieving precise control of film thickness and uniformity, particularly on rough as-built AM surfaces. Variations in local thickness can promote stress development, cracking during drying, or incomplete coverage of microstructural features, thereby limiting long-term protective performance.

Alternative surface coatings are for example plasma-polymerized siloxane¹¹⁴ and metallic gold-nickel coatings⁵⁴.

Overall, the literature demonstrates that a wide range of coating and surface modification strategies can significantly improve the corrosion resistance of additively manufactured AlSi10Mg alloys. Oxide-based treatments such as anodization and PEO provide substantial reductions in corrosion current density and enhanced barrier properties, while sol–gel and plasma-polymerized coatings offer thin-film alternatives with promising chemical stability.

However, a recurring limitation across all strategies is their sensitivity to the heterogeneous microstructure and rough surface condition inherent to the additively manufactured state.¹⁰¹ Melt pool boundaries, silicon-rich networks, porosity, and surface cavities influence coating nucleation, growth kinetics, and defect formation. As a result, incomplete film formation, micro-pores, interfacial discontinuities, and thickness inhomogeneities remain critical factors governing long-term performance.¹⁰⁹ Even strategies that show substantial short-term improvements may be compromised by localized electrolyte penetration along microstructural interfaces.¹¹⁵

These findings underline that corrosion protection of AM AlSi10Mg cannot rely solely on conventional coating approaches transferred from wrought or cast alloys. Instead, successful

protection requires deliberate interfacial engineering that accounts for microstructural anisotropy, oxide chemistry, and electrochemical heterogeneity. The challenge therefore lies not only in selecting an appropriate coating system, but in designing protection concepts that are intrinsically compatible with the unique structural features of additively manufactured aluminum alloys.

2.2.2. Aluminum alloy 2024

AW2024 is among the most important high-strength aluminum alloys used in lightweight structural applications. The principal alloying element is copper, which plays a central role in strengthening the alloy through precipitation hardening mechanisms.¹¹⁶ Industrial production of AW2024 began in the early 1920s, primarily to meet the demands of the emerging aerospace industry.¹⁶ The long history of this alloy reflects the extensive body of research and practical experience that has accumulated over more than a century.

It is particularly noteworthy that, despite having been developed over 100 years ago, AW2024 continues to be widely used as a structural material and remains an active subject of scientific investigation. Current research efforts focus predominantly on corrosion protection strategies and on the development of functional surface modifications and coating systems capable of addressing its chemically heterogeneous microstructure. A defining characteristic of AW2024 is the presence of intermetallic particles, which create local electrochemical heterogeneities and act as preferential sites for micro-galvanic corrosion. The complex distribution, composition, and electrochemical activity of these intermetallic phases make corrosion control and homogeneous surface functionalization particularly challenging.

The structure of the present section follows the approach adopted in Section 2.2.1. First, the manufacturing route of the AW2024 alloy used in this thesis is briefly described. Subsequently, the characteristic microstructural features are correlated with the corrosion behavior of the alloy. Finally, selected corrosion protection strategies are critically reviewed and discussed in the context of their applicability to AA/AW2024.

2.2.2.1. Principle manufacturing process and resulting microstructure

Conventionally produced aluminum alloys are generally classified into cast alloys and wrought alloys. Wrought alloys are designated by a four-digit numbering system, in which the first digit indicates the alloy series. The alloy investigated in this thesis, AW2024, begins with the number “2”, which denotes copper as the principal alloying element. The second digit, “0”, indicates that this alloy is not a modification of a preceding 2024 alloy. By contrast, alloy 2124 would represent the first modification of alloy 2024. The final two digits indicate the specific alloy within that series.¹¹⁷

Wrought aluminum alloys can further be divided into strain-hardenable and age-hardenable materials. Although all aluminum alloys can in principle be strengthened by strain hardening, only selected alloy systems are suitable for age hardening. In particular, the 2xxx, 6xxx, and 7xxx series belong to the group of age-hardenable aluminum alloys.⁵⁰

The fundamental objective of age hardening is to maximize the mechanical strength of the alloy, such that strength levels comparable to those of unalloyed steels can be achieved while maintaining the low density required for lightweight structural applications.¹¹⁶ The temper

designation of age-hardenable aluminum alloys is indicated by the letter “T”, followed by one to five digits.⁵⁰ The AW2024 alloy used in this thesis was subjected to a T3 temper condition. This means that the alloy was first solution heat-treated, then cold worked (strain-hardened), and subsequently naturally aged at room temperature (RT).¹¹⁸ For the sake of simplicity, the temper designation of the AW2024 alloy used is no longer stated, except where it is specifically addressed.

During solution heat treatment, the alloy is heated to a temperature just below the solidus line. At approximately 548 °C, copper reaches its maximum solubility in aluminum. The alloy is then rapidly cooled, for example by water quenching. This processing step, referred to as quenching, must be performed as quickly as possible after solution treatment in order to retain the alloying elements, in the case of AW2024 primarily copper, in a supersaturated solid solution.¹¹⁸ Since this rapid cooling step often causes distortion, a controlled plastic deformation is commonly applied afterward, typically in the form of approximately 2% strain hardening. The alloy is then allowed to age at room temperature. During this aging process, the supersaturated solid solution progressively decomposes, leading to the precipitation of alloying elements at grain boundaries.¹¹⁶ It is this precipitation process that ultimately gives the alloy its high strength and its characteristic microstructure.⁵⁰

In addition to the precipitation processes described above, the resulting microstructure of AA2024-T3 is characterized by a highly heterogeneous distribution of intermetallic particles embedded within the aluminum matrix. These particles originate from both solidification and subsequent thermomechanical processing steps and are not uniformly distributed across the alloy.

A detailed microstructural analysis reveals that AW2024-T3 contains a wide range of intermetallic phases with varying compositions, sizes, and morphologies. The most prominent phases include S-phase (Al_2CuMg) and θ -phase (Al_2Cu), as well as Fe- and Mn-containing particles such as $\text{Al}_7\text{Cu}_2\text{Fe}$ and $\text{Al}_3(\text{Cu,Fe,Mn})$. Importantly, many intermetallic particles are not single-phase but exhibit a multiphase character, consisting of compositional subdomains within a single particle.¹¹⁹ This reflects complex precipitation and solidification pathways and contributes to a highly heterogeneous local chemistry. Figure 12 shows a digital microscope image of the AW2024 surface investigated in this thesis, illustrating the large number of intermetallic particles present on the surface.

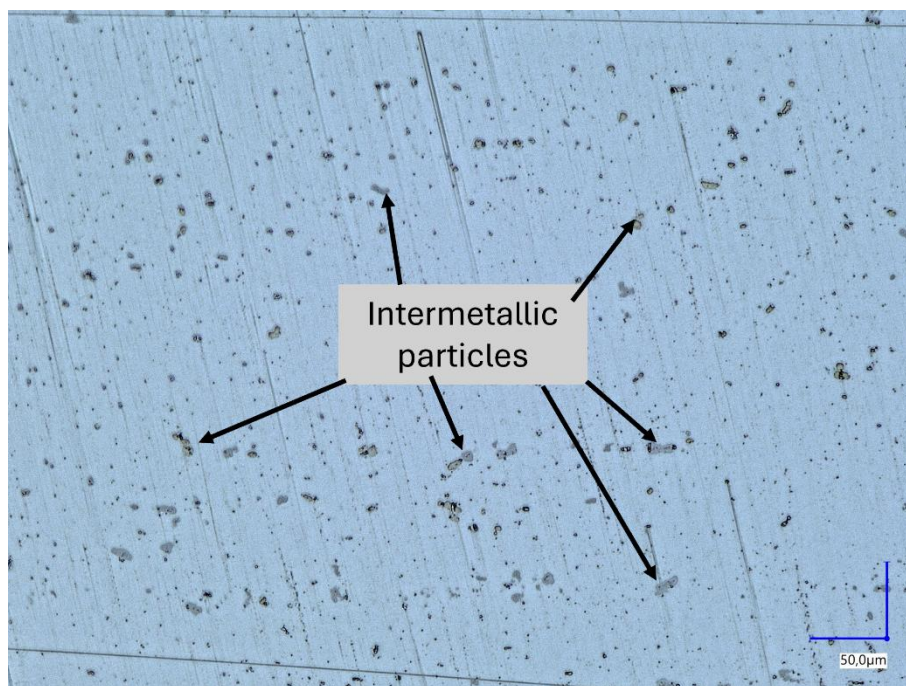


Figure 12. Typical microscopic image of the AW2024 surface used in this thesis. The surface was polished and etched prior to imaging. Intermetallic particles can be identified by their darker contrast relative to the Al matrix. Some of them are indicated by arrows.

Furthermore, intermetallic particles are frequently surrounded by compositional “periphery zones”, which differ chemically from both the particle core and the surrounding matrix. These regions are enriched in elements such as Cu and Mg and are considered to play a significant role in localized corrosion processes, as they can influence local electrochemical activity and promote trenching phenomena.¹¹⁹ The presence of such chemically graded interfaces further increases the complexity of the microstructure.

In terms of spatial distribution, intermetallic particles exhibit a broad size range, with the majority of particles being smaller than 5 μm, while larger particles occur less frequently. Additionally, clustering of intermetallic particles is commonly observed, leading to local variations in particle density and electrochemical activity across the surface.¹¹⁹ This spatial inhomogeneity implies that the local ratio of anodic to cathodic sites may vary significantly depending on the observed surface area.

Overall, the microstructure of AW2024-T3 can be described as a complex, multiphase system with pronounced chemical and spatial heterogeneity. This heterogeneity is a key factor governing the corrosion behavior of the alloy, as it promotes microgalvanic coupling and localized breakdown of the passive film.

2.2.2.2. Correlation between microstructure and corrosion behavior

Based on the microstructural characteristics described in the previous section, the corrosion behavior of AW2024 can be directly related to the pronounced chemical and spatial heterogeneity of the alloy. In particular, the presence of intermetallic particles with distinct electrochemical properties introduces local galvanic interactions between the particles and the surrounding

aluminum matrix, which govern both the initiation and propagation of localized corrosion processes.

The intermetallic phases present in AW2024-T3, including S-phase (Al_2CuMg), θ -phase (Al_2Cu), and Fe- and Mn-containing particles such as Al-Cu-Fe-Mn and Si-containing intermetallics, exhibit different electrochemical potentials relative to the matrix.^{11,23,119} Some selected corrosion potentials of the as-mentioned phases are summarized in Table 1.

Table 1. Corrosion potential values for selected intermetallic phases as commonly present in Al alloys. The table is adapted from Ref.¹¹. The stoichiometries and E_{corr} values were originally reported in Ref.²³ and measured in 0.1 M NaCl solution. For improved comparability with the electrochemical measurements presented in this thesis, the originally reported potentials vs SCE were additionally converted to the SHE scale using $E_{\text{SHE}} = E_{\text{SCE}} + 0.244 \text{ V}$.¹²⁰

Stoichiometry	E_{corr} vs V_{SCE}	E_{corr} vs V_{SHE}
Al	-0.823	-0.579
Al-2%Cu	-0.672	-0.428
Al_2Cu	-0.665	-0.421
Mg_2Si	-1.538	-1.294
Al_2CuMg	-0.883	-0.639
$\text{Al}_7\text{Cu}_2\text{Fe}$	-0.551	-0.307
$\text{Al}_{20}\text{Cu}_2\text{Mn}_3$	-0.565	-0.321
Al_3Fe	-0.539	-0.295
Mg_2Al_3	-1.013	-0.769

As already discussed in Section 2.1.3.2, these phases establish local anodic and cathodic sites at the microscale. In general, Fe- and Mn-rich intermetallics are more noble than the aluminum matrix and therefore act as local cathodes (see Figure 6).

Among the different intermetallic phases, the S-phase (Al_2CuMg) is particularly important for the initiation of localized corrosion. It is initially anodic relative to the aluminum matrix and undergoes rapid dealloying in chloride-containing environments, characterized by the preferential dissolution of Mg and Al (see Figure 7).¹²¹ This process results in the formation of a Cu-rich remnant. As the dealloying progresses, the electrochemical behavior of the particle changes, and the Cu-enriched remnant becomes more noble than the surrounding matrix. Consequently, the

particle undergoes a transition from anodic to cathodic behavior. This polarity reversal enables the particle to sustain cathodic reactions and thereby promotes further dissolution of the adjacent matrix, leading to the formation of trenches at the particle–matrix interface.^{27,121} This sequence of anodic dissolution followed by cathodic activation represents a key mechanism linking the microstructure to corrosion propagation.⁵⁷ In addition, the electrochemical response of Al₂CuMg is reported to be highly variable and dependent on environmental conditions, indicating that the phase exhibits a metastable behavior during corrosion.¹²²

In contrast, the θ -phase (Al₂Cu) is inherently more noble than the aluminum matrix and predominantly acts as a cathodic phase throughout exposure. It is characterized by a stable passive behavior over a wide potential range and is capable of sustaining cathodic reactions such as oxygen reduction.¹²² As a consequence, θ -phase particles promote localized dissolution of the surrounding matrix through galvanic coupling rather than through significant self-dissolution. This behavior is consistently described in the literature, where Al₂Cu is identified as a stable cathodic constituent that contributes to localized corrosion susceptibility.^{27,57}

In addition to the electrochemical properties of individual phases, the spatial distribution of intermetallic particles plays a critical role. As described in the previous section, intermetallic particles in AW2024-T3 are not uniformly distributed but often occur in clusters and may exhibit compositional gradients at their peripheries.¹¹⁹ This implies that the local ratio of anodic to cathodic sites can vary significantly across the surface. As a result, localized corrosion processes are not confined to isolated particles but rather evolve through interactions between neighboring particles. These coupled processes can ultimately lead to the transition from metastable to stable localized corrosion.

Overall, the corrosion behavior of AW2024 can therefore be understood as a direct consequence of its heterogeneous intermetallic microstructure. The S-phase acts as a primary initiation site due to its initial anodic dissolution and subsequent polarity reversal, whereas the θ -phase and Fe-rich intermetallics function as stable cathodic sites that sustain matrix dissolution. The interplay between these phases, together with their spatial arrangement, determines the extent and progression of localized corrosion.

2.2.2.3. Corrosion protection strategies and challenges

The pronounced microstructural and electrochemical heterogeneity of AW2024 not only governs its corrosion behavior but also fundamentally constrains the effectiveness of conventional corrosion protection approaches. In particular, the coexistence of anodic and cathodic intermetallic phases, together with their spatial clustering and compositional variability, leads to highly localized electrochemical activity that cannot be effectively mitigated by uniform barrier-type coatings alone.

Consequently, corrosion protection strategies for AW2024 must not only provide a physical barrier against electrolyte ingress, but also address the local electrochemical activity associated with intermetallic particles and chemically heterogeneous surface regions.¹²³

Historically, chromate conversion coatings have represented one of the most applied and versatile corrosion protection strategies for AW2024 and related aerospace aluminum alloys.⁵⁰ Their outstanding performance is commonly attributed to the combined action of barrier formation and active corrosion inhibition, since soluble chromate species can migrate toward damaged regions and promote re-passivation.¹²⁴ For this reason, chromate-based systems have

long served as the technological benchmark against which newer protection strategies are compared. However, due to the toxicity and regulatory restrictions associated with hexavalent chromium compounds, substantial research has focused on the development of chromate-free alternatives.¹²³

Among the chromate-free approaches, anodizing remains one of the most established methods for improving the corrosion resistance of AW2024. In aerospace applications, sulfuric acid anodizing and tartaric-sulfuric acid anodizing have received particular attention as industrially relevant alternatives to chromic acid anodizing. Nevertheless, the performance of anodic films on AW2024 is strongly influenced by the underlying intermetallic microstructure. Local differences in oxide growth kinetics at Cu-rich and Fe-rich intermetallic particles may lead to structural inhomogeneities, interfacial defects, and preferential weak points within the anodic layer. As a result, anodizing can significantly improve corrosion resistance, but its long-term effectiveness remains coupled to the heterogeneous substrate chemistry of the alloy.³³

This coupling between substrate heterogeneity and coating performance is also evident in post-treated anodic systems. For example, it has been shown that the corrosion resistance of tartaric-sulfuric acid anodized AW2024-T3 can be further improved by Ce-containing post-treatments, indicating that the performance of the anodic film can be enhanced by additional chemical stabilization and partial sealing of structurally weak regions.¹²⁵ Similarly, hybrid sol-gel top layers applied to anodized AW2024-T3 have been reported to increase the resistive properties of the porous anodic structure and delay the access of aggressive species to the barrier layer.¹²⁶

Similar to AM AlSi10Mg substrates, also PEO coating has emerged a promising coating strategy for AW2024 surfaces, particularly when combined with subsequent sealing steps. At the same time, the intrinsic porosity and discharge-induced defects of PEO coatings represent a major challenge, since they may act as transport pathways for aggressive species. For this reason, PEO on AW2024 is often discussed not as a standalone solution, but as part of duplex protection systems in which the porous oxide is further sealed or functionalized.¹⁰⁷

Sol-gel and hybrid sol-gel coatings represent an important class of such surface modification strategies. On AW2024, sol-gel-based systems have been studied both as direct protective coatings and as top layers on anodized substrates. Their main advantage lies in the possibility of combining barrier protection with chemical functionality, for example by improving interfacial bonding, sealing defects, or incorporating inhibitor species. However, their performance depends strongly on film uniformity, defect density, and compatibility with the heterogeneous oxide chemistry of the substrate. This is particularly relevant for AW2024, where local variations in oxide composition and intermetallic distribution may influence coating formation and adhesion at the microscale.^{126,127}

In addition to oxide-based and hybrid barrier systems, inhibitor-containing organic coatings and conversion layers have been widely investigated for AW2024. In this context, rare-earth-based systems and lithium-based inhibitor concepts have received considerable interest. Their general aim is not merely to isolate the alloy from the environment, but to suppress the electrochemical processes responsible for localized attack, particularly in the vicinity of intermetallic particles or coating defects. Active inhibitors can therefore complement purely barrier-based protection by addressing those local sites where uniform coatings may be insufficient.^{128,129}

Overall, the literature shows that a wide range of corrosion protection strategies can improve the performance of AA/AW2024, including conversion coatings, anodizing, PEO, and sol-gel or organic hybrid systems. However, the effectiveness of these approaches is often limited by the

chemically and electrochemically heterogeneous nature of the alloy surface. This implies that the main challenge in protecting AA/AW2024 is not only to form a stable coating, but to achieve robust protection across a surface that contains multiple intermetallic phases, local galvanic couples, and spatially varying oxide chemistries. Consequently, current research increasingly focuses on multifunctional and chemically tailored protection concepts that can address this heterogeneity more effectively than conventional uniform coating strategies.^{107,123,129}

2.3. Molecular adsorption and thin film concepts for corrosion protection

In addition to conversion coatings, oxide films, and thicker organic barrier concepts, corrosion protection can also be achieved by molecular and nanometric surface modifications. In such systems, the protective function no longer arises primarily from geometric thickness, but from the controlled adsorption, anchoring, and lateral organization of molecules or ultrathin films at the metal surface. This makes the chemistry of the metal–coating interface, the packing density of the adsorbates, and the resulting defect structure decisive parameters for barrier performance and long-term stability. In this sense, such approaches can be understood as a form of surface engineering, in which corrosion protection is achieved through the deliberate modification of interfacial chemistry and nanoscale surface properties rather than through coating thickness alone.^{36,37}

At this length scale, film formation is governed by the interplay between molecule–substrate interactions and lateral intermolecular interactions. Depending on the adsorption chemistry and molecular architecture, adsorbates may form ordered monolayers, polymer-grafted surface layers, or ultrathin inorganic barrier films. For self-organizing systems in particular, the balance between adsorption strength, surface mobility, and intermolecular cohesion determines whether a compact and well-ordered interphase can develop. Such organization is essential because densely packed films reduce the accessibility of water, oxygen, and aggressive ions to the substrate and thereby suppress the elementary processes of corrosion. At the same time, molecular adsorption processes are inherently sensitive to the local chemical nature of the substrate. This is particularly relevant for chemically heterogeneous alloy surfaces, where differences in oxide composition, hydroxylation state, or intermetallic distribution may locally influence molecular anchoring and film organization. Molecular self-assembly therefore offers the possibility of selectively addressing chemically distinct surface sites, although the resulting film quality remains strongly dependent on the local interfacial chemistry.^{35–37}

Accordingly, this section first discusses the fundamentals of molecular adsorption on metal surfaces, with particular emphasis on the adsorption and self-assembly of molecular layers. It then addresses polymeric surface grafting using PDMS as a flexible organic nanolayer concept, before turning to inorganic SiO_x thin films as dense nanometric barrier layers. Together, these approaches illustrate how corrosion protection can be engineered through interfacial chemistry and nanoscale film architecture rather than coating thickness alone.

2.3.1. Fundamentals of self-assembling monolayers (SAMs) on metal surfaces

In general, adsorption processes on metal surfaces may be broadly differentiated into physisorption and chemisorption. Physisorption is based on comparatively weak non-covalent interactions, such as van der Waals forces, electrostatic interactions, or hydrogen bonding, and is therefore usually reversible and strongly influenced by the surrounding environment. Chemisorption, in contrast, involves the formation of stronger and more specific interfacial bonds between the adsorbate and the substrate and therefore provides the basis for stable and persistent surface modification. For corrosion protection, chemisorption is of particular importance because it allows functional molecules to remain anchored to the substrate even under aqueous or chemically aggressive conditions.^{37,40}

Usually, the usage of SAMs is intended to chemisorb on the surface of choice to build a reliable new interface. A self-assembled molecular layer is typically composed of amphiphilic molecules with a modular architecture consisting of three functional parts: a surface-active head group, a molecular backbone or spacer, and a terminal group (see Figure 13). The head group controls the chemical anchoring to the substrate, the backbone largely determines lateral packing and structural cohesion within the film, and the terminal group defines the physicochemical properties of the outer interface, such as polarity, wettability, and chemical reactivity. This modularity makes self-assembled layers particularly attractive for surface engineering, because interfacial bonding and outer surface functionality can be adjusted independently to a considerable extent.^{39,40}

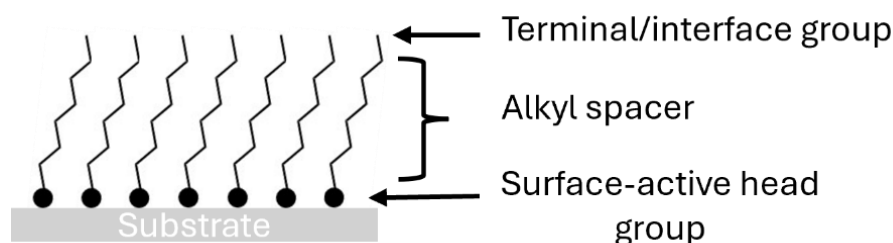


Figure 13. General structure of a SAM. Own illustration, adapted from Ref⁴⁰.

The development of structural order in such films is driven by the minimization of the total interfacial free energy. After initial adsorption, the molecules may reorganize on the surface in order to maximize favorable intermolecular interactions and to occupy energetically preferred adsorption sites. In alkyl-substituted systems, van der Waals interactions between neighboring chains play a particularly important role in stabilizing compact arrangements. The result is often a densely packed monolayer in which the molecular chains adopt a defined tilt angle relative to the surface normal rather than remaining fully upright. The existence of such tilt angles reflects the compromise between head-group spacing imposed by the substrate and chain packing preferences imposed by intermolecular cohesion.⁴⁰ The tilt angle can be derived from PM-IRRAS data by the following formula⁸² rearranged for ODPA⁸⁵:

$$\frac{I_{CH_2}}{I_{CH_3}} = \frac{2n \cdot \cos^2(90^\circ - \alpha)}{3 \cdot \cos^2(35^\circ - \alpha)} \quad (2-20)$$

with I_i as the intensity of the respective CH_x valence vibration bands, n as the number of methylene groups in the alkyl chain (for ODPa $n = 17$) and α as the angle between the surface normal and the alkyl chain axis. For ODPa adsorption on physical vapor-deposited Al on Si wafers, which may be regarded as an idealized Al surface in contrast to the inhomogeneous Al-alloy surfaces investigated in this thesis, Maxisch et al. reported an α value of approximately 17.3° .⁸⁵ For an AlMg1 alloy, Bram et al. found an α value of approximately 31° for the same molecule after 66 h of adsorption.⁸²

Another important value used to qualitatively describe the conformational order of SAMs is the IR-band position of the asymmetric and symmetric methylene stretching vibrations ($\nu_{as}CH_2$ and ν_sCH_2 , respectively). It has been proposed that the lower the wavenumber of these bands, the higher the conformational order of the alkyl chains.¹³⁰ Spori et al. reported that alkyl chains containing more than 15 carbon atoms adopt a more ordered crystalline-like structure after sufficient adsorption time, with $\nu_{as}CH_2$ and ν_sCH_2 bands appearing at approximately 2920 and 2850 cm^{-1} , respectively.¹³⁰

The self-assembly process is not instantaneous, but proceeds through several stages. Initially, molecules adsorb to available surface sites. This is followed by nucleation of locally ordered domains, subsequent domain growth, and reorganization of less favorably arranged adsorbates. The adsorption and self-organization process is schematically illustrated in Figure 14. During this process, defects such as vacancies, grain boundaries, misoriented domains, and low-density regions may gradually be reduced, although they are rarely eliminated completely. The final film structure thus depends not only on molecular design, but also on kinetic factors such as deposition time, concentration, solvent, temperature, and post-treatment. Even in the classical thiol/gold model system, the formation of highly ordered monolayers is understood as a dynamic process involving chemisorption of the thiolate species, lateral diffusion, and progressive structural annealing at the interface.^{40,131}

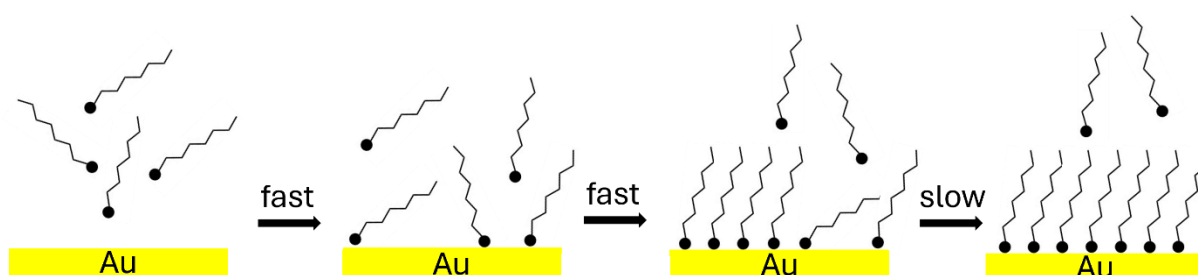


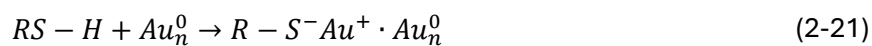
Figure 14. General adsorption and self-assembly process of alkanethiol on gold surfaces. Own illustration, adapted from Ref.⁴⁰.

Because of this dynamic character, the term self-assembly does not imply that every adsorbed layer is automatically highly ordered. Rather, the degree of order depends on how effectively the adsorbate system can reorganize after binding. Strong chemisorption alone is not sufficient if the molecules are immobilized before lateral packing can occur. Likewise, strong intermolecular attraction alone does not guarantee a stable film if the head group does not provide sufficiently

robust anchoring to the substrate. A well-ordered self-assembled layer is therefore the result of a balanced coupling between interfacial bond formation and lateral molecular mobility. This aspect is especially important for corrosion protection, because structural defects introduced during assembly may become preferential pathways for the ingress of water, oxygen, or aggressive ions like chlorides.^{36,39}

The classical literature on self-assembled monolayers is dominated by alkanethiol systems on gold, because these provide comparatively well-defined substrates and permit detailed structural characterization. These systems established the fundamental concept that nanometer-thick molecular films can develop crystalline-like order, distinct chain tilt angles, and chemically defined terminal surfaces.

In the classical model system of alkanethiols on gold, adsorption proceeds through chemisorption of the sulfur head group accompanied by cleavage of the S–H bond. The adsorbed species is therefore generally described as a thiolate rather than an intact thiol. Ulman describes this process formally as oxidative addition of the S–H bond to the gold surface followed by reductive elimination of hydrogen, with the released hydrogen commonly assumed to recombine to H₂ on a clean gold surface. The resulting interfacial species is commonly described as a gold(I) thiolate adsorbed on metallic gold (Au(0)), and the strong Au–S interaction forms the basis of the well-known thiol-derived self-assembled monolayers on noble metals. Experimental evidence from XPS, IR, Raman spectroscopy, and electrochemical studies supports the conclusion that the adsorbing species is the thiolate rather than the intact thiol.^{39,40}



For aluminum-based materials, however, this model system cannot be transferred directly. Under ambient conditions, aluminum is covered by a native oxide film, and molecular adsorption therefore occurs not on metallic Al, but on a hydroxylated aluminum oxide surface. As a consequence, the relevant chemisorption mechanism differs fundamentally from the thiol/gold case. On hydroxylated oxide surfaces, phosphonic acids bind through condensation reactions between the phosphonic acid head group and surface hydroxyl groups. In the case of aluminum oxide, this leads to the formation of alumino-phosphonate linkages via Al–O–P bonds, accompanied by elimination of water. A representative reaction may be written as



This chemistry makes phosphonic acids particularly attractive for functionalization of oxidized aluminum surfaces.⁴³

Importantly, the phosphonic acid head group can bind to the oxide surface in different coordination motifs. Depending on the local surface chemistry and deposition conditions, mono-, bi-, or tridentate binding modes may occur, depending on whether one, two, or all three oxygen atoms of the phosphonate group participate in interfacial bonding. The coexistence of different binding motifs has been discussed repeatedly in literature, and the distribution of these binding

states is influenced by factors such as molecular structure, deposition procedure, surface hydroxylation, and increasing chain ordering during film growth. It has even been suggested that tridentate coordination may evolve toward lower coordination states at higher surface coverage as intermolecular packing constraints become more important.⁴³

The adsorption of phosphonic acids on aluminum oxide must therefore be regarded as a substrate-specific interfacial reaction rather than a simple generic self-assembly process. Since the oxide surface provides hydroxyl groups as reaction partners, the density, distribution, and reactivity of these groups directly influence molecular anchoring. In addition, the resulting film structure is strongly affected by the assembly pathway. Molecular dynamics studies of ODPa on hydroxyl-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) have shown that the solvent plays a decisive role in both adsorption kinetics and final monolayer organization. In these simulations, successful binding events were associated with hydrogen bonding of the phosphonic acid anchor to surface hydroxyl groups, followed by proton transfer, water elimination, and switching to the strongly bound deprotonated phosphonate state. This indicates that the assembly of phosphonate monolayers on oxide surfaces is controlled not only by the intrinsic affinity of the head group to the surface, but also by solvent structuring, interfacial hydrogen bonding, and the accessibility of vacant binding sites during growth.¹³¹

From the perspective of corrosion protection, these mechanistic differences are highly relevant. A strongly bound but poorly organized adsorbate layer may still contain a substantial density of defects or loosely packed regions that permit the transport of water, oxygen, or aggressive ions toward the substrate. Conversely, a densely packed and well-ordered molecular film can significantly reduce the accessibility of the metal surface even if the total thickness remains in the nanometre range. The corrosion-inhibiting properties of molecular films therefore do not simply arise from the presence of adsorbed molecules, but from the formation of a compact and chemically stable molecular interphase that modifies transport processes, interfacial wettability, and local electrochemical reactions at the metal/electrolyte interface.^{35,36}

At a more general level, molecular adsorption may therefore be understood as a form of interfacial surface engineering. By selecting appropriate anchor groups, molecular backbones, and terminal functionalities, it becomes possible to tailor not only the stability of the adsorbed layer, but also the physicochemical nature of the resulting outer surface. In this way, nanoscale surface modification can be used to control wettability, interfacial energy, accessibility of corrosive species, and the local electrochemical response of the substrate. At the same time, the quality of such molecular interphases remains highly sensitive to the chemical heterogeneity of the underlying surface. On heterogeneous alloy substrates, local variations in oxide composition, hydroxylation state, or intermetallic distribution may affect adsorption strength and molecular organization on the microscale. Molecular adsorption therefore offers the possibility of addressing surface properties at the scale of the underlying heterogeneity, but its success depends strongly on the compatibility between adsorbate chemistry and substrate chemistry.^{37,39,43}

2.3.2. Polymeric surface grafting: Polydimethylsiloxane (PDMS)

PDMS is one of the most widely used silicone materials and represents a particularly interesting polymeric surface modifier for corrosion-related applications. Structurally, PDMS consists of an inorganic siloxane backbone with repeating Si–O–Si units and two methyl side groups bound to each silicon atom (see Figure 15). This hybrid inorganic–organic architecture gives rise to a

characteristic combination of properties, including high conformational flexibility, low glass transition temperature, low surface tension, and pronounced water repellency. At the same time, the methyl-rich outer surface reduces intermolecular interactions and contributes to the low surface energy of PDMS-modified interfaces. These physicochemical features make PDMS highly attractive for surface engineering concepts in which wetting, interfacial adhesion, and accessibility of corrosive media are to be controlled by nanometric surface modification rather than by thick coating architectures.^{44,45}

From the perspective of surface modification, PDMS is particularly interesting because it may be grafted to oxidic surfaces by different routes, including both UV-induced grafting and spontaneous room-temperature grafting. These two approaches are mechanistically distinct, but both provide viable routes to the formation of thin hydrophobic interphases on oxide-covered metallic substrates. In both cases, the resulting protective function does not arise from bulk coating thickness, but from the generation of a nanometric, chemically bound, low-surface-energy surface layer that alters wetting and restricts interfacial access of corrosive media.^{44,46}

In the UV-induced grafting route it is proposed that, irradiation promotes bond cleavage within the PDMS molecule and thereby generates reactive species that can be immobilized on inorganic substrates. Tesler et al. showed that this concept can be applied to a broad range of metals, metal oxides, and ceramics, yielding thin PDMS-based surface layers without the need for additional photocatalysts or complex multistep pretreatments. Based on DFT analysis, the authors argued that Si–C bond cleavage is energetically favored over scission of the siloxane backbone under the applied UV conditions (UV-B light), thereby enabling surface activation while largely preserving the polymer chain architecture. Depending on the processing conditions, the resulting surface may function either as a covalently grafted low-surface-energy layer or, in combination with excess silicone oil, as a lubricant-retaining interphase. Importantly, UV-grafted PDMS layers were also reported to improve corrosion resistance on metallic substrates by shifting corrosion potentials to more positive values and reducing corrosion current densities.⁴⁶

In parallel, several studies have shown that PDMS can also become covalently attached to oxide surfaces without external activation and already at room temperature. This spontaneous grafting pathway is particularly notable because silicones have long been regarded as comparatively inert materials. Teisala et al. demonstrated that methyl-terminated PDMS can bond spontaneously to silicon oxide surfaces at room temperature, resulting in transparent hydrophobic films with thicknesses in the nanometer range. The proposed mechanism involves hydrolysis of siloxane bonds in PDMS through nucleophilic attack of water, generating silanol-terminated chain fragments. These hydroxyl-terminated species can subsequently undergo condensation reactions either with surface silanol groups or with other hydrolyzed PDMS fragments, thereby enabling the formation of covalently attached Si–O–Si linkages at the interface. The proposed reaction pathway is also shown in Figure 15. The principals of this reaction pathway has also been postulated in earlier studies by Krumpfer and McCarthy.⁴⁵ They additionally showed that linear silicones can react with other inorganic oxide surfaces such as aluminum, titanium or nickel. Thus, room-temperature grafting of PDMS provides an alternative immobilization route in which interfacial reaction is driven by the chemistry of the oxide surface and the local water environment rather than by external irradiation.⁴⁴ However, it should be noted that the spontaneous grafting strategy takes significantly longer (≈ 24 h) compared to the UV-B grafting strategy by Tesler et al (≈ 30 minutes).

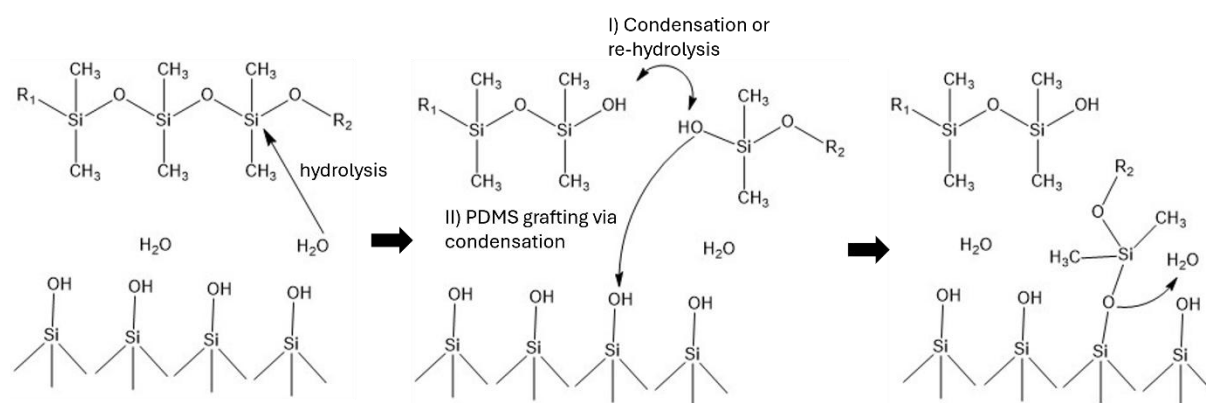


Figure 15. Water-assisted (spontaneous) grafting of PDMS on water/hydroxyl-terminated silicon surfaces. Adapted from Teisala et al.⁴⁴

Nevertheless, in this context, the spontaneous binding of PDMS to oxidic surfaces can be regarded as conceptually related to the adsorption processes discussed in the previous section. Even though PDMS is polymeric and does not possess a classical low-molecular-weight anchoring group, its interaction with hydroxylated oxide surfaces likewise proceeds through an interfacial reaction sequence that depends on surface chemistry, water availability, and molecular mobility. Marinova et al. described the hydrophobization of glass by PDMS adsorption as a two-stage process. In the first stage, a comparatively rapid physical adsorption occurs, which was attributed to hydrogen-bond-mediated interaction between PDMS and surface silanol groups, resulting in a dense but dynamic physisorbed monolayer. In the second stage, a slower grafting process takes place in which chemically bound PDMS species are formed through reaction of hydroxyl-terminated PDMS with surface silanol groups. This distinction between initial adsorption and subsequent chemical fixation is particularly valuable for understanding PDMS as an interfacial surface modifier, since it places the system close to the conceptual framework of molecular adsorption and self-organization discussed for thinner molecular films.¹³²

With respect to corrosion protection, PDMS can influence electrochemical processes through several coupled mechanisms. First, grafted PDMS reduces the surface energy and thereby increases hydrophobicity, which may lower electrolyte retention and shorten the time of wetness under atmospheric exposure. This aspect is particularly relevant for thin electrolyte layer corrosion, where wetting behavior strongly affects local electrolyte geometry, oxygen access, and salt concentration (see Section 2.1.4.3). Second, the grafted polymer layer introduces a nanometric barrier that hinders direct contact between the substrate and the environment, thereby slowing the transport of water, dissolved oxygen, and aggressive ions toward the interface. Third, the flexible polymeric nature of PDMS allows the formation of comparatively defect-tolerant interphases, especially on rough or chemically heterogeneous surfaces, although prolonged contact with water may eventually lead to hydrolytic degradation or electrolyte permeation. Teisala et al. explicitly noted that prolonged direct contact with water can ultimately degrade such PDMS coatings.⁴⁴

Tesler et al. reported that UV-grafted PDMS layers on metallic substrates decreased corrosion current densities and shifted corrosion potentials to more positive values in chloride-containing electrolyte, indicating suppressed electrochemical activity at the interface. In droplet-based exposure tests, PDMS-infused surfaces also reduced the corroded area fraction compared with unmodified metallic surfaces, which points to a delayed initiation and limited spreading of

corrosive media. These findings suggest that UV-induced PDMS grafting is particularly effective in situations where corrosion is coupled to wetting, droplet mobility, or localized electrolyte exposure.⁴⁶

Overall, PDMS represents a polymeric surface grafting concept that occupies an intermediate position between molecular adsorption and conventional polymer coatings. Its relevance lies not in the formation of thick barrier films, but in the ability to create nanometric, chemically bound, low-surface-energy interphases directly on oxide-covered substrates by different grafting routes. Both UV-induced and spontaneous room-temperature grafting provide viable strategies to immobilize PDMS on such surfaces and thereby modify wetting, reduce interfacial accessibility of corrosive media, and suppress early-stage electrochemical processes, particularly under atmospheric or short-term exposure conditions. This makes PDMS a particularly useful model system for understanding how polymeric grafting can be used as a nanoscale corrosion protection strategy.

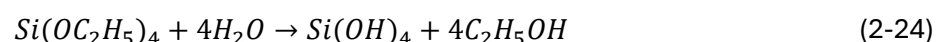
2.3.3. Inorganic barrier layers: SiO_x thin films

In addition to molecular and polymeric surface modifications, corrosion protection may also be achieved by the formation of ultrathin inorganic barrier layers. In the context of the present work, particular interest lies in silica-based thin films derived from tetraethyl orthosilicate (TEOS) in the presence of ammonia. Such films are chemically related to the classical Stöber process¹³³, but differ in their growth mode. Whereas the conventional Stöber process is typically associated with the formation of colloidal silica particles in the bulk solution, the process relevant here is directed toward the formation of a surface-bound SiO₂/SiO_x layer on a substrate via CVD. The underlying hydrolysis–condensation chemistry is similar, but the reaction pathway is shifted from homogeneous nucleation in the liquid phase to heterogeneous nucleation and network growth at or near the solid surface. Oh et al. explicitly described direct silica film formation from TEOS/ethanol/aqueous ammonia solutions as a heterogeneous nucleation process on a hydrophilic surface under conditions intermediate between stable solution and gel formation.¹³⁴

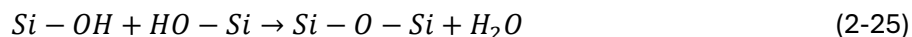
From a chemical point of view, the film formation is initiated by the base-catalyzed hydrolysis of TEOS. In aqueous media, ammonia establishes an alkaline environment according to



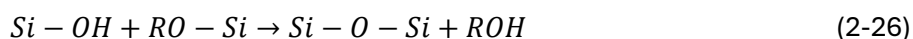
and thereby increases the concentration of nucleophilic hydroxide species. Under such conditions, the silicon center in TEOS becomes susceptible to nucleophilic attack, which facilitates hydrolysis of the ethoxy groups and promotes the formation of silanol-containing intermediates. In simplified form, the complete hydrolysis of TEOS may be written as



although in reality the reaction proceeds stepwise through partially hydrolyzed alkoxysilane species. The subsequent condensation of silanol groups leads to formation of the siloxane network:



and, if partially hydrolyzed species are still present,



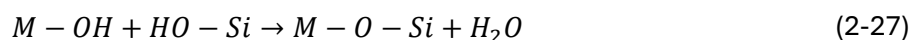
with $R = \text{C}_2\text{H}_5$ in the TEOS-derived system. In alkaline media, not only hydrolysis but also condensation is promoted because deprotonated silanol species are highly nucleophilic and can attack silicon centers in neighboring molecules or oligomers. Ammonia therefore does not simply accelerate a single elementary step, but shifts the overall hydrolysis–condensation sequence toward the formation of a crosslinked silica network. This base-catalyzed mechanism is well established for alkoxysilane polymerization in general and underlies the Stöber chemistry specifically.¹³⁵

If this chemistry proceeds predominantly in the bulk phase, silica particles are formed, corresponding to the classical Stöber process. If, however, heterogeneous nucleation at a hydrophilic substrate is favored, the same reaction sequence can result in direct thin-film growth. This distinction is particularly important for corrosion-relevant silica coatings. Oh et al. showed that dense silica films can be deposited directly from basic TEOS solutions at temperatures below 60 °C, and concluded that growth and densification occur simultaneously during deposition.¹³⁴ Kákoš et al. reported a closely related route in which adsorbed TEOS multilayers were subsequently reacted with mixed $\text{H}_2\text{O}/\text{NH}_3$ vapors at atmospheric pressure and room temperature, yielding homogeneous ultrathin silica films without vacuum equipment or high-temperature sintering.¹³⁶ These authors explicitly distinguished the desired surface-bound film growth from the homogeneous particle nucleation that characterizes the classical Stöber route.^{134,136}

With respect to terminology, a distinction should be made between SiO_2 and SiO_x . SiO_2 refers to ideally stoichiometric silica, whereas SiO_x is a broader term that includes sub-stoichiometric or compositionally variable silicon oxide networks. In practice, thin films prepared from alkoxysilane precursors at relatively mild temperatures may not be perfectly stoichiometric, especially if residual hydroxyl groups, incompletely condensed species, or organic remnants remain in the network. In the present context, both terms are therefore relevant: the films are silica-derived and chemically silica-like, but their exact stoichiometry and condensation state may depend on the deposition conditions and post-treatment.

The attachment of such silica-derived films to metallic substrates is generally mediated by the native oxide or hydroxide-covered surface rather than by direct bonding to the metallic phase. On hydroxylated metal oxide surfaces, hydrolyzed silanol species may condense not only with one

another, but also with surface hydroxyl groups, thereby forming interfacial metal–oxygen–silicon linkages. In a simplified form, this interfacial grafting step may be represented as



where M-OH denotes a hydroxylated oxidic surface site. This surface condensation reaction is similar to the PDMS-grafting mechanism discussed in the previous section. Accordingly, the developing SiO₂/SiO_x layer is not merely deposited physically onto the substrate, but can become chemically linked to the oxidized metal surface.¹³⁷ For the present system, this means that the silica-derived film is expected to nucleate and grow preferentially at hydroxylated, hydrophilic surface regions, which directly couples substrate surface chemistry to film adhesion and continuity. This interpretation is fully consistent with the heterogeneous nucleation model proposed for TEOS/ammonia-derived silica films on hydrophilic substrates.^{134,136}

The structure and protective quality of the resulting films depend strongly on the balance between network formation, densification, and defect generation. Dense and homogeneous silica films can provide effective barrier properties because they reduce the transport of water, dissolved oxygen, and aggressive ions to the underlying metal surface.

The thickness of silica-derived barrier layers is an important parameter because corrosion protection at this length scale depends less on bulk thickness than on film continuity, densification, and defect density. The used TEOS-based CVD-deposition system in this thesis results in a silica or silica-like film typically in the nanometer range. Deng et al. reported a silica shell thickness of approximately 25 nm after 24 h, demonstrating that Stöber-like vapor-assisted silica formation can generate well-defined nanoscale oxide layers.¹³⁸ In addition, Teisala et al. reported a film thickness of approximately 3 nm after a 4 h TEOS-based CVD process.⁴⁴ Taken together, these results indicate that the relevant thickness scale of such SiO₂/SiO_x barrier layers lies well below the micrometer regime, such that film continuity and interfacial integrity become more important than geometric thickness alone.

Oh et al. reported that TEOS/ammonia-derived films exhibited refractive index, hydroxyl content, and hardness values similar to those of calcined sol–gel silica films, indicating that relatively compact silica-like networks can be achieved even at comparatively mild temperatures. Likewise, Kákoš et al. showed that ultrathin silica layers prepared from adsorbed TEOS and H₂O/NH₃ vapor displayed acceptable insulating properties, including a breakdown field of 5.4 MV·cm⁻¹ which points to a coherent and functionally effective oxide barrier.^{134,136}

For corrosion protection, these features are highly relevant. The protective action of SiO₂/SiO_x thin films is based primarily on their barrier function. In contrast to self-assembled molecular layers or grafted PDMS films, which modify interfacial chemistry and wetting through thin organic structures, silica-derived films act as inorganic transport barriers with comparatively high chemical stability. Their effectiveness therefore depends on film continuity, low porosity, sufficient densification, and robust adhesion to the oxidized substrate.¹³⁹ This also explains why even nanometric silica films can improve electrochemical performance: if the layer is sufficiently compact, it may significantly delay electrolyte penetration and suppress interfacial charge transfer despite its limited thickness. A related example is provided by silica-based TEOS/ammonia-derived coatings on aluminum-SiC composites, which were reported to improve

corrosion resistance in NaCl-containing media when a sufficiently continuous silica network was formed.¹⁴⁰

Overall, TEOS/ammonia-derived $\text{SiO}_2/\text{SiO}_x$ thin films may be understood as inorganic barrier layers formed by a Stöber-like hydrolysis–condensation chemistry that is redirected toward surface-bound film growth. The chemically decisive features are the ammonia-catalyzed hydrolysis of TEOS, the subsequent condensation of silanol species into a siloxane network, and the possibility of interfacial condensation with hydroxylated substrate surfaces. The key mechanistic distinction relative to the classical Stöber process therefore lies not in the elementary chemistry itself, but in the transition from homogeneous particle nucleation to heterogeneous film formation at the substrate. The resulting silica-derived interphases can form compact, chemically linked barrier layers that suppress the transport of corrosive species and thereby complement molecular adsorption and polymer grafting strategies in nanoscale corrosion protection.

2.4. Surface and interface analytical methods

As discussed in the previous sections, the corrosion protection strategies investigated in this work are based on chemical modification and structural control of the outermost surface region. Their functionality therefore depends not only on the bulk properties of the substrate, but primarily on the composition, bonding state, thickness, morphology, and wettability of nanoscale surface and interfacial layers. In consequence, their characterization requires analytical methods that are capable of probing these properties with sufficient surface sensitivity and chemical specificity.

This is particularly important for molecularly adsorbed layers, polymer-grafted interphases, and ultrathin inorganic barrier films, where the relevant structural and chemical changes are often restricted to only a few nanometers from the substrate surface. In such systems, the successful formation of the desired interphase cannot be assessed by a single method alone, but instead requires a combination of complementary techniques. Depending on the respective analytical principle, information may be obtained on elemental composition, chemical bonding, film thickness, surface topography, wetting behavior, or electrochemical response.

The following sections therefore introduce the analytical methods used in this work and briefly discuss their underlying principles, information depth, and specific relevance for the characterization of surface-modified aluminum alloys. Particular emphasis is placed on methods that allow the identification of chemical surface functionalities, the assessment of interfacial film formation, and the correlation of surface properties with corrosion-related performance.

2.4.1. Spectroscopic methods for chemical surface analysis

Spectroscopic methods are generally based on the interaction of electromagnetic radiation with matter. Depending on the energy of the incident radiation and the nature of the material system, this interaction may lead to absorption, emission, reflection, scattering, or photoelectron excitation. The resulting spectral response provides information on the chemical composition, electronic structure, bonding state, or molecular organization of the investigated material. These principles form the basis of a wide range of analytical methods used for chemical surface

analysis. The following sections briefly describe the spectroscopic methods applied in this thesis and explain their specific relevance for the intended analyses.

2.4.1.1. (PM)-IRRAS

Infrared reflection–absorption spectroscopy (IRRAS) is a vibrational spectroscopic method for the characterization of thin films and adsorbed species on reflective metal substrates. In contrast to transmission infrared (IR) spectroscopy, the infrared beam is directed onto the metal surface and the spectral information is obtained from the reflected radiation. This reflection geometry makes IRRAS particularly suitable for surface-confined molecular layers, because the interaction of the incident electromagnetic field with the reflective metal substrate enables the detection of very thin adsorbate films. The sensitivity of the method is highest at grazing incidence, where the electromagnetic field distribution at the metal interface becomes especially favorable for probing surface species. For thin films on highly reflective metals, the measured reflectance change can be treated in linear approximation and is approximately proportional to the film thickness and absorption coefficient, which makes IRRAS particularly suitable for ultrathin interfacial layers.^{141,142}

The surface sensitivity of IRRAS is closely linked to the polarization of the incident radiation. S-polarized light is defined as light whose electric field vector is oriented perpendicular to the plane of incidence, i.e. parallel to the sample surface. In contrast, p-polarized light has its electric field vector within the plane of incidence and therefore contains a component normal to the surface. At a reflective metal surface, these two polarization states behave differently upon reflection. For s-polarized light, the tangential electric field at the surface is strongly attenuated because the reflected wave undergoes a phase inversion, leading to near-cancellation of the field. In contrast, p-polarized light retains a significant electric field component normal to the surface, particularly at grazing incidence. As a consequence, vibrational modes with a transition dipole moment component oriented along the surface normal are preferentially excited. The process described is illustrated schematically in Figure 16. This behavior originates from the surface selection rule¹⁴³ of IRRAS, which makes the method sensitive not only to the chemical composition of organized surface films, but also to their molecular orientation.^{141,144}

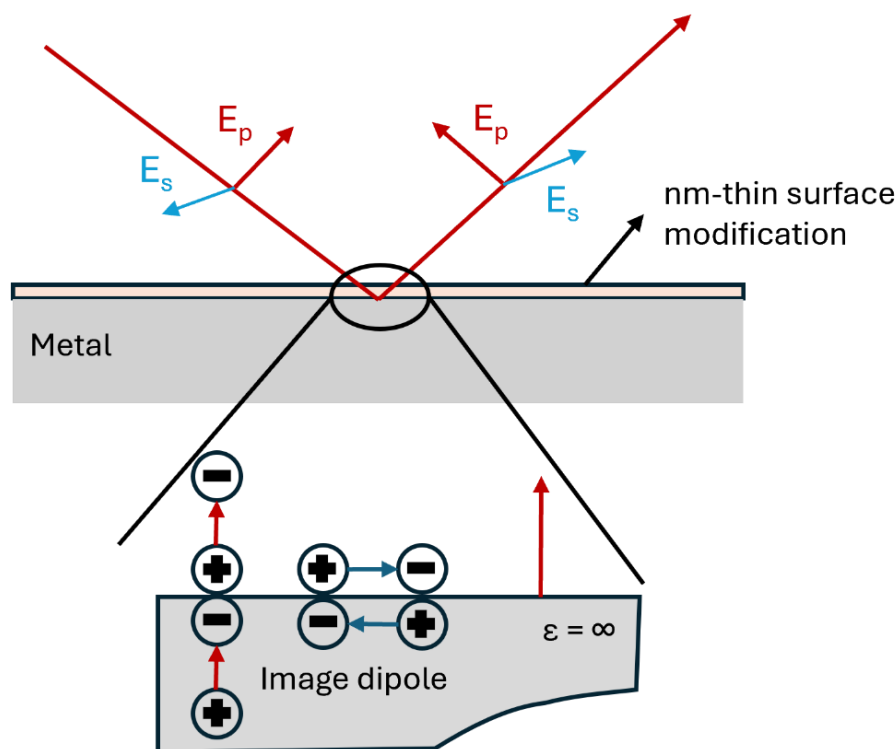


Figure 16. Physical concept of polarization-modulated (PM) IRRAS: The p-component of electric field adds to a non-zero vector after reflection, while the electric field of the s-component gets cancelled. Own illustration, adapted from Ref¹⁴¹.

The orientational sensitivity of IRRAS can be described in general form by

$$I(\omega) \sim |\vec{\mu} \cdot \vec{E}|^2, \quad (2-28)$$

where $I(\omega)$ is the intensity of absorption of radiation at the frequency ω , $\vec{\mu}$ is the transition dipole moment and $\vec{E}$ is the electric field vector at the surface. Under IRRAS conditions on metal substrates, the relevant field component is predominantly directed along the surface normal. Consequently, the intensity of a given vibrational band depends directly on the orientation of the vibrating group relative to the substrate surface.¹⁴⁵

Polarization-modulation IRRAS (PM-IRRAS) builds directly on these principles. Instead of measuring the reflected intensity for one fixed polarization state, the technique rapidly modulates the polarization of the incident infrared beam between p- and s-polarization, typically by means of a photoelastic modulator (PEM). More explicitly, a linear polarizer is used to generate a well-defined input polarization before the beam enters the photoelastic modulator. The PEM then periodically changes the phase relation between two orthogonal field components, which results in a modulated polarization state and thus enables differential detection of the p- and s-polarized surface response. In a simplified form, the PM-IRRAS signal may be written as

$$S = C \frac{R_p - R_s}{R_p + R_s} J_2(\tau_0), \quad (2-29)$$

where S is the PM-IRRAS signal, C is a constant, J_2 is the second-order Bessel function of the maximum dephasing τ_0 introduced by the amplitude of mechanical modulation of the PEM and R_p and R_s are the p- and s- polarized reflectances of the sample. Since the p-polarized component contains the surface-sensitive spectral contribution whereas the s-polarized component is largely suppressed at the metal surface, the differential signal selectively enhances the response of surface-bound species. PM-IRRAS can therefore be understood as a differential form of IRRAS in which the polarization dependence of the reflection process is used directly as the analytical contrast mechanism.^{141,144,145}

The main advantage of PM-IRRAS is that it strongly reduces spectral contributions from isotropic background phases. Species in the surrounding gas phase or in isotropic bulk media absorb largely independent of the polarization direction and therefore contribute similarly to both the p- and s-polarized signals. Their contribution is thus largely canceled in the differential measurement, whereas the signal from anisotropically adsorbed surface species is retained. In addition, PM-IRRAS improves the detectability of ultrathin interfacial layers and does not require a separate clean reference measurement in the same way as conventional reflection measurements.^{141,142,144}

These advantages are particularly relevant for the thin-film systems investigated in the present work. Molecularly adsorbed layers, grafted PDMS films, and related nanometric interphases are all confined to the outermost surface region and often possess thicknesses of only a few nanometres or less. Their successful characterization therefore requires a method that combines chemical specificity with high surface sensitivity and efficient suppression of background contributions. PM-IRRAS fulfills these requirements particularly well.

2.4.1.2. XPS

XPS is a surface-sensitive spectroscopic method for the chemical analysis of solid materials. The technique is based on the photoelectric effect, in which irradiation with monochromatic X-rays leads to the emission of electrons from core or valence levels. In laboratory-based XPS, the emitted electrons are most commonly excited by Al K α or Mg K α radiation, and their kinetic energies are measured by an electron energy analyzer. The corresponding binding energy is then obtained from

$$BE = h\nu - KE - \Phi, \quad (2-30)$$

where BE is the binding energy, $h\nu$ the photon energy, KE the measured kinetic energy of the photoelectron and Φ the spectrometer work function. This relationship is illustrated in the form of an energy level diagram in Figure 17. Because core-level binding energies are characteristic of the emitting element, XPS enables elemental identification. In addition, small shifts in binding energy caused by the local chemical environment give rise to so-called chemical shifts, which

form the basis for chemical-state analysis. With the exception of hydrogen and helium, all elements can in principle be detected by XPS.^{146,147}

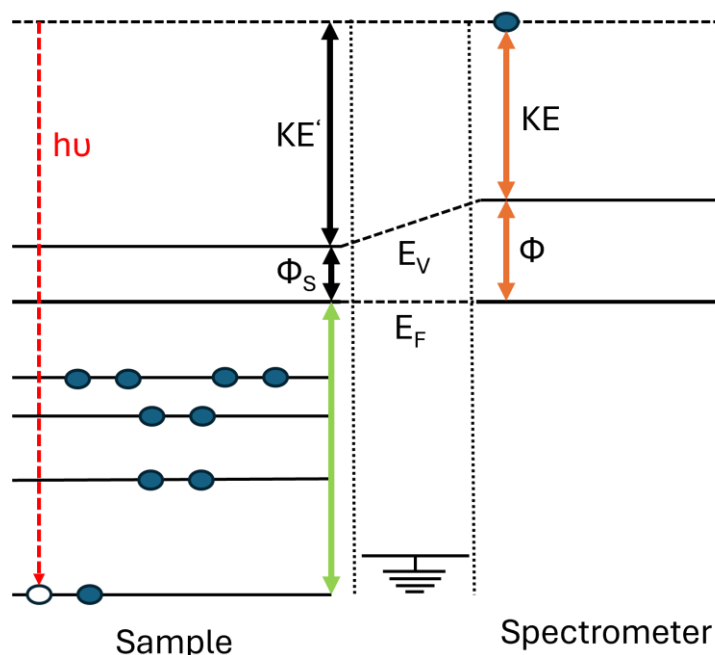


Figure 17. Principle of XPS analysis by energy level diagram. Own illustration, adapted from Ref¹⁴⁸.

The pronounced surface sensitivity of XPS originates from the limited escape depth of electrons in condensed matter. Although the incident X-rays penetrate far into the sample, only those photoelectrons that leave the solid without significant inelastic energy loss contribute to the characteristic photoelectron peak. The intensity of these unscattered electrons decreases approximately exponentially with depth according to

$$I(d, \theta) = I_0 \exp\left(-\frac{d}{\lambda \cos \theta}\right), \quad (2-31)$$

where d is the depth of photoelectron origin, λ is the inelastic mean free path (IMFP) of the photoelectrons and θ is the emission angle with respect to the surface normal. The corresponding information depth is therefore angle dependent and is commonly approximated as about $3\lambda \cos \theta$ which contains approximately 95% of the detected signal. As a consequence, decreasing the take-off angle relative to the surface normal enhances surface sensitivity, whereas normal emission probes somewhat deeper into the material. This angle dependence is the basis of angle-resolved XPS and is of particular importance for thin films and layered surface structures.^{146,147}

In addition to elemental identification, XPS provides information on the chemical state of the emitting species. Changes in oxidation state, coordination, or bonding environment lead to measurable shifts in core-level binding energies and often also influence peak shapes. XPS spectra may further exhibit spin-orbit splitting, shake-up or shake-off satellites, and multiplet

structures, depending on the electronic structure of the investigated material. Quantitative analysis is usually based on the comparison of background-corrected peak areas after normalization with appropriate sensitivity factors and instrumental transmission corrections. The reliability of such analysis depends strongly on physically consistent peak fitting, energy referencing, and a clear understanding of the intrinsic and extrinsic contributions to the spectrum.^{146,149}

For thin oxide layers on metals, XPS can also be used for approximate film-thickness determination by means of a uniform overlayer model. A practically important example is the method proposed by Strohmeier for estimating the oxide thickness on aluminum alloys from a single Al2p spectrum. In this approach, the ratio of the oxidic and metallic Al2p peak intensities is related to the oxide thickness according to

$$d_o = \lambda_o \cdot \sin\theta \cdot \ln \left[\frac{N_m \lambda_m I_o}{N_o \lambda_o I_m} + 1 \right], \quad (2-32)$$

where d_o is the oxide thickness, I_o and I_m are the intensities of the oxidic and metallic Al2p signals, N_o and N_m are the atomic volume densities in the oxide and the metal, respectively, λ_o and λ_m are the corresponding IMPs of oxidic and metallic components.¹⁵⁰ Strohmeier showed that this approach allows estimation of aluminum oxide thicknesses from a single ESCA/XPS measurement without sputter depth profiling or separate calibration procedures. For conventional Al and Mg X-ray sources, the practically accessible maximum oxide thickness is limited to approximately three times the inelastic mean free path, which corresponds to about 7.5-8.5 nm for the Al/Al oxide system.¹⁵⁰

For the present work, XPS is particularly relevant because the investigated corrosion protection strategies are based on nanoscale interfacial modifications. The method enables determination of the elemental composition and chemical state of the outermost surface region and is therefore well suited to identify native and modified oxide layers, adsorbed SAMs, PDMS-derived surface films, and silica- or silicon oxide-based interphases on aluminum substrates. XPS therefore provides a central analytical link between interfacial chemistry, thin-film formation, and corrosion-relevant surface properties in the systems investigated in this thesis.

2.4.1.3. ToF-SIMS

ToF-SIMS is a highly surface-sensitive mass spectrometric method that provides detailed chemical information from the outermost surface region of a material. Owing to an information depth of typically less than 2 nm, the technique is particularly well suited for the analysis of surface chemistry, adsorbed species, and chemically modified near-surface layers. In addition to mass spectra, ToF-SIMS can provide lateral chemical images with high spatial resolution as well as depth profiles and three-dimensional chemical maps. A further advantage of the method is that it generally does not require extensive sample pretreatment such as labeling, coating, or matrix addition.¹⁵¹

The basic principle of ToF-SIMS is based on the bombardment of a surface with a pulsed primary ion beam. In the present case, secondary ions are generated by pulsed Bi_x^+ cluster ions, which are

particularly suitable for surface-sensitive chemical analysis because they provide high secondary-ion yields while preserving molecular information more effectively than many monatomic ion sources. The impact of the primary ions transfers energy to the near-surface region and induces the emission of secondary particles, including electrons, neutrals, photons, and positive as well as negative secondary ions. Only the secondary ions are detected mass-spectrometrically. Since these ions originate from the outermost atomic and molecular layers, the resulting spectra reflect the chemical composition of the sample surface with very high surface sensitivity. Depending on the chemical nature of the sample, both elemental ions and molecular fragment ions can be detected, so that ToF-SIMS provides not only elemental but also structural and molecular information.^{151,152}

In the time-of-flight analyzer, all emitted secondary ions are accelerated through a defined potential and thus acquire the same kinetic energy. The ion velocity then depends on the mass-to-charge ratio, so that lighter ions travel faster through the field-free drift region and reach the detector earlier than heavier ions. This relationship is described by

$$zE = \frac{1}{2}mv^2 \quad (2-33)$$

and

$$L = vt, \quad (2-34)$$

which can be combined to give

$$\frac{m}{z} = \frac{2Et^2}{L^2}, \quad (2-35)$$

where z is the ion charge number, E the accelerating voltage, m the ion mass, v the ion velocity, L the flight path length, and t the time of flight. The measured flight time can therefore be converted directly into a mass-to-charge ratio. In this way, ToF-SIMS records a complete mass spectrum of the sputtered secondary ions.¹⁵¹

A key distinction in SIMS analysis is that between static and dynamic measurement conditions. Under static conditions, the primary ion dose is kept sufficiently low so that only a very small fraction of the outermost surface is affected, which minimizes beam-induced damage and preserves chemical structure as far as possible. This mode is particularly useful for the chemical characterization of the original outermost surface. By contrast, depth profiling requires deliberate and continuous removal of material by sputtering. In this case, the sample surface is sequentially eroded and chemical information is recorded as a function of sputter time or converted depth, allowing the composition of layered or graded near-surface regions to be investigated.^{151,152}

In the present work, ToF-SIMS was employed for the spectrometric characterization of AW2024 surfaces and for depth profiling using a Cs^+ sputter source. In such measurements, the analytical information is obtained from repeated cycles of surface erosion and spectral acquisition. The Bi_x^+ cluster beam is used for secondary-ion generation and mass analysis, whereas the Cs^+ beam progressively removes material from the surface between analysis cycles. This enables the chemical composition to be followed as a function of depth and is therefore particularly useful for the investigation of thin surface films, interfacial enrichment, oxide layers, and chemically modified subsurface regions. Cs^+ sputtering is especially relevant when negative secondary ions are of interest, since cesium implantation into the near-surface region can enhance the yield of negative ions and thereby improve the detectability of electronegative species.

For metallic materials such as AW2024, ToF-SIMS depth profiling offers the important advantage that chemical gradients across the outermost surface region can be resolved with high sensitivity. At the same time, the technique remains strongly matrix dependent, meaning that ion yields are influenced not only by elemental concentration but also by the local chemical environment. Consequently, ToF-SIMS data are generally interpreted semi-quantitatively unless appropriate reference materials or calibration procedures are available. Nevertheless, the method is highly valuable for identifying characteristic secondary ions, comparing relative signal intensities, and locating interfaces or chemically distinct layers within the near-surface region.^{151,152}

Overall, ToF-SIMS combines extremely high surface sensitivity with molecular and elemental specificity and the possibility of depth-resolved analysis. In the context of the present thesis, the method is particularly suitable for examining the chemical composition of modified model AlCu5.9 surfaces and for tracking how this composition changes with depth under Bi_x^+ -assisted analysis and Cs^+ -assisted sputter profiling.

2.4.2. Microscopic methods for surface characterization

While spectroscopic methods primarily provide chemical and electronic information about the outermost surface region, microscopic methods are used to obtain spatially resolved information on surface morphology, topography, and structural heterogeneity.

2.4.2.1. Digital microscopy

The fundamental operating principle of optical microscopy is based on the magnified imaging of small objects by an optical system. In a conventional light microscope, light reflected from or transmitted through the specimen is collected by the objective lens and projected through the optical path to produce an enlarged image. In classical microscope designs, this magnified intermediate image is further enlarged by the eyepiece (i.e. ocular) and observed directly by the human eye. In this way, objects that are too small to be resolved (usually $< 75 \mu\text{m}$)¹⁵³ or evaluated reliably by unaided vision can be visualized and examined in greater detail.

The magnification and image quality of the microscope are primarily determined by the optical components, especially the objective lens, as well as by the illumination geometry and the focusing conditions. Thus, the following equation can be used to define the resolution limit

$$d_{min} = k_1 \frac{\lambda}{NA}, \quad (2-36)$$

with k_1 defined as the coherence factor, which is dependent on the exposure wavelength and varies between 0.55 and 0.8. The numerical factor NA is defined as

$$NA = n \cdot \sin(\alpha), \quad (2-37)$$

with α depicting the aperture angle.¹⁴⁵

As a result, optical microscopy provides spatially resolved information on surface morphology, structural inhomogeneities, defects, and local damage features in the dimension of microns. For corrosion-related investigations, this is particularly useful for the rapid visualization of corrosion spots, cracks, deposits, delamination phenomena, or local coating defects.

Digital microscopy extends this classical optical principle by replacing or supplementing direct visual observation with digital image acquisition. Instead of being viewed exclusively through an eyepiece, the optically magnified image is projected onto a semiconductor-based detector, typically a complementary metal oxide semiconductor sensor, where it is converted into an electronic signal. This signal is then processed by dedicated hardware and software and displayed digitally. In this way, digital microscopy combines the imaging principle of light microscopy with electronic image processing and computer-assisted analysis.¹⁵⁴

The digital processing of the acquired image enables additional possibilities for surface characterization beyond simple visual inspection. These include image storage and documentation, contrast enhancement, dimensional measurements, automated image stitching, depth-of-field extension by focus stacking, and in some systems also height reconstruction or three-dimensional surface visualization. Digital microscopy therefore represents a particularly useful method for the rapid and nondestructive characterization of surface morphology over comparatively large sample areas.¹⁵⁴

For the present work, digital microscopy is mainly used as a complementary method for the visualization of surface features and corrosion-related morphological changes. Additionally in the case of rough, as-built AlSi10Mg specimen, three-dimensional images are used to extract line profiles. These line profiles are then used to calculate the mean absolute deviation of the line-profile heights from the mean line (R_a), according to the definition of the arithmetical mean deviation of the roughness profile in ISO 21920-2:2021¹⁵⁵

$$R_a = \frac{1}{n} \sum_{i=1}^n |z_i - \bar{z}|, \quad (2-38)$$

where n is the number of evaluated data points in the line profile, z_i is the height value of the profile at data point i and $\bar{z}$ is the mean value of all height values in the profile.

In combination with the spectroscopic and electrochemical methods described above, it provides an important link between chemical surface modification and the visible manifestation of surface damage or coating inhomogeneity.

2.4.2.2. SEM and EDS

Scanning electron microscopy (SEM) is a microscopic technique in which a finely focused electron beam is scanned raster-wise across the specimen surface. In contrast to conventional optical or transmission-based imaging, the image is generated serially, point by point, from signals emitted by the specimen during electron irradiation. The electron-optical column typically comprises an electron source, condenser lenses, scan coils, and an objective lens that focuses the incident beam into a small probe on the sample surface. In modern instruments, this probe diameter is typically in the nanometer range, and field-emission sources enable particularly small probe sizes and thus improved spatial resolution.¹⁵³ The experimental set-up of a typical SEM is schematically shown in Figure 18.

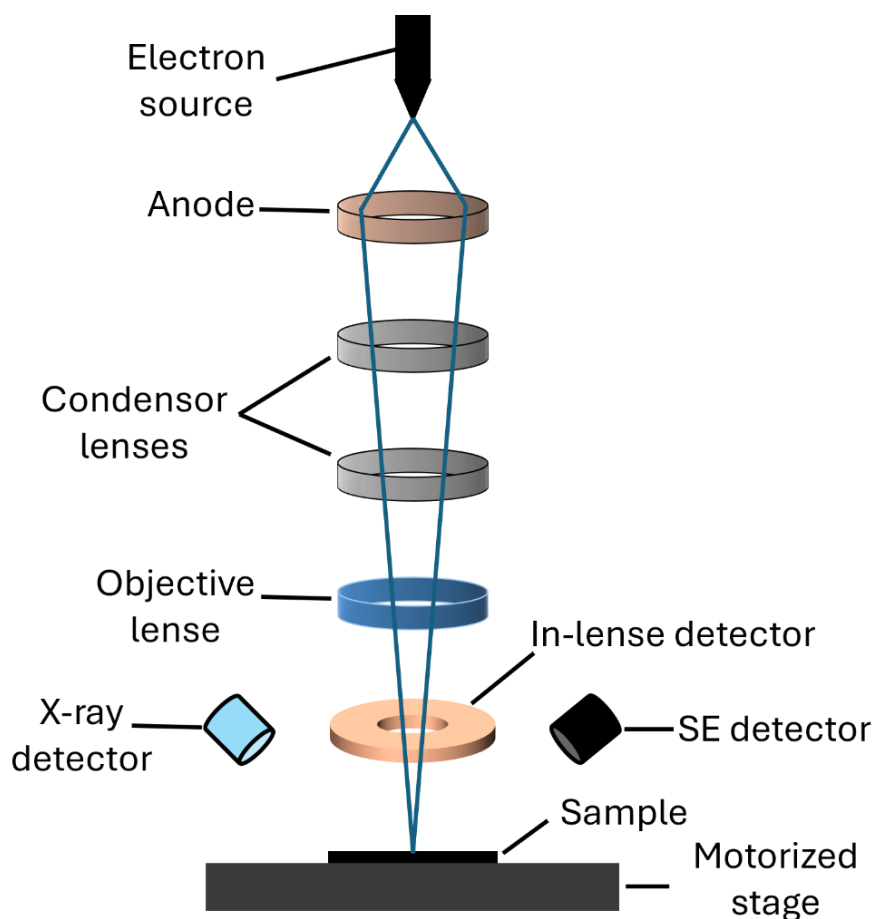


Figure 18. Schematic drawing of the main components of an SEM microscope with X-ray detection possibility. Own illustration, adapted from Ref.¹⁵⁶.

When the primary electrons enter a bulk specimen, they undergo both elastic and inelastic scattering, giving rise to an interaction volume beneath the surface. Different signals can be

generated from this interaction volume. Most commonly, SEM imaging is based on secondary electrons (SE) or backscattered electrons (BSE). Secondary electrons are low-energy electrons generated by inelastic scattering and can escape only from the near-surface region, typically within a depth of about 1–2 nm. As a result, SE images are particularly sensitive to surface topography and fine morphological details. The In-lense detector only measures the SE originating from the primary electron beam, which are called “SE1”. They have a high topographical but a low element specific contrast. “SE2” are generated by BSE, thus they have a certain element specific contrast. The “SE-detector” measures SE1 as well as SE2. Backscattered electrons, by contrast, originate from elastic scattering of the primary beam and are associated with a larger interaction volume. They are therefore especially useful for compositional contrast and for distinguishing regions of different average atomic number.¹⁵³

A characteristic advantage of SEM is its comparatively high spatial resolution combined with a large depth of focus. This makes the method particularly suitable for the examination of rough or structured surfaces, where features located at different heights may remain simultaneously visible with good apparent sharpness. In comparison with light microscopy, SEM therefore provides substantially improved resolution and is especially valuable for the morphological characterization of coatings, surface defects, deposits, and localized corrosion features on bulk metallic specimens.¹⁵³

Energy dispersive X-ray spectroscopy (EDS) is commonly coupled with SEM in order to obtain elemental information from the irradiated region. Its physical basis is the emission of characteristic X-rays following inner-shell ionization of atoms by the incident electron beam. When a core-level vacancy is created, it is filled by an electron from a higher shell, and the released energy is emitted as an X-ray photon whose energy is characteristic of the respective element. The emitted photons are detected by a semiconductor detector, where their energy is converted into electron–hole pairs and subsequently processed into an energy spectrum. The position of the peaks allows elemental identification, whereas their intensity can be used, within limits, for semiquantitative or quantitative analysis.¹⁵³

In practice, EDS spectra contain not only characteristic peaks but also a continuous bremsstrahlung background, and their interpretation is limited by finite detector resolution, peak overlap, dead-time effects, and possible spurious signals originating from the surrounding instrument geometry or nearby sample regions. Nevertheless, the combination of SEM and EDS provides a powerful and widely used approach for correlating local morphology with local elemental composition. In the context of the present work, SEM is primarily used to visualize surface morphology whereas EDS serves as a complementary method for identifying elemental distributions associated with surface domains.

2.4.2.3. AFM and SKPFM

AFM is a scanning probe technique in which a sharp tip attached to a microfabricated cantilever is brought into close proximity to a sample surface. The tip–sample interaction alters the cantilever response, and this change is used as the feedback signal during scanning. By adjusting the vertical position of the sample or cantilever such that the interaction is maintained at a preset level, the instrument reconstructs the surface topography from the corresponding z-displacement. Since the recorded image reflects the trajectory of the tip apex, the measured topography represents a convolution of the real surface with the tip geometry; consequently,

lateral dimensions are influenced by the finite tip radius, whereas height information is generally more reliable.¹⁵⁷

A typical AFM system consists of the cantilever probe, a deflection detection unit, a feedback controller, and piezoelectric scanners for x-, y-, and z-motion. In many instruments, cantilever deflection is detected by the optical beam deflection method, in which a laser beam reflected from the back side of the cantilever is projected onto a position-sensitive photodiode. Depending on the operating mode, AFM can be performed either in contact mode, where the tip remains in continuous contact with the surface, or in AC mode, where the cantilever oscillates near resonance and the tip interacts only intermittently with the sample.¹⁵⁷ The principle set-up of an AFM measurement is shown in Figure 19.

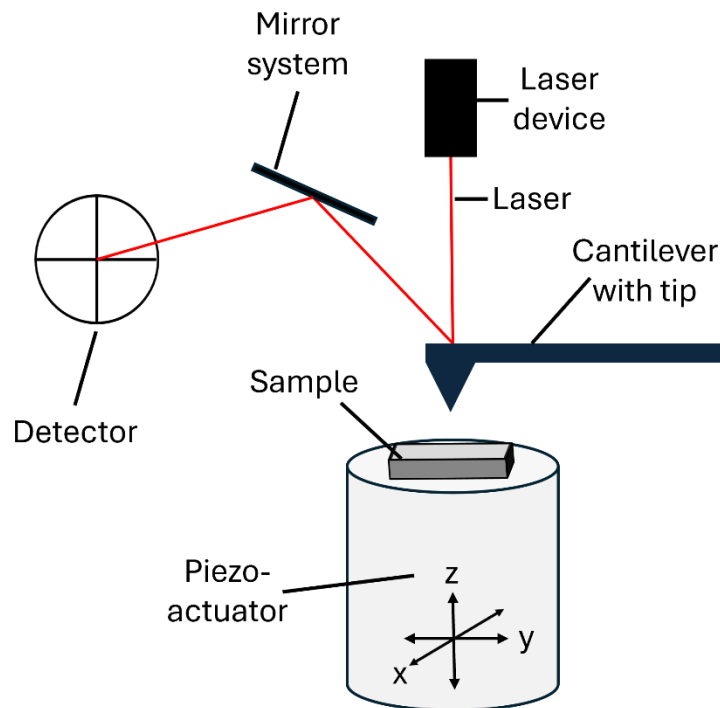


Figure 19. Schematic of a principle AFM set-up. Cantilever displacement due to tip-sample interactions is measured by a laser beam that is reflected from the cantilever onto a photodetector system. The sample topography is raster-scanned by a piezoactuator. Own illustration, adapted from Ref.⁸¹.

These operating modes differ not only in signal generation but also in the nature of the tip-sample interaction. In contact mode, the cantilever is not externally oscillated and the measured deflection directly reflects the applied force, which may be approximated as

$$F = k_c z \quad (2-39)$$

where k_c is the cantilever spring constant and z the cantilever deflection. Because the tip remains in continuous contact with the surface during lateral scanning, the interaction is dominated by repulsive contact forces, and additional lateral drag forces may occur. In AC or tapping-type

modes, by contrast, the oscillating tip approaches and leaves the surface periodically, so that both attractive and repulsive interaction contributions may occur depending on oscillation amplitude, set-point, and surface properties. Within this description, attractive tip-sample interactions decrease the cantilever resonance frequency, whereas repulsive interactions shift the resonance to higher frequencies.¹⁵⁷

The cantilever itself can be described, to first approximation, as an elastic beam. For a rectangular cantilever with length L , width w , thickness d and Young's modulus E , the spring constant is given by

$$k_c = \frac{3EI}{L^3} = \frac{Ewd^3}{4L^3}, \quad (2-40)$$

where I is the area moment of inertia. In dynamic operation, the cantilever behaves as a resonant oscillator. For the first eigenmode, the effective mass is approximately $m_{\text{eff}} \approx 0.24 m$, and the corresponding angular frequency may be expressed as

$$w_1 = \sqrt{\frac{\beta_1^4 k_c}{3m}}, \quad (2-41)$$

with $\beta_1 = 1.875$. These relationships illustrate that AFM contrast is fundamentally governed by the mechanical response of the cantilever to local surface forces.¹⁵⁷

SKPFM extends AFM by adding a spatially resolved measurement of the local electrical potential difference between a conductive tip and the sample surface. When two dissimilar materials are brought into electrical interaction, their Fermi levels equilibrate, which gives rise to a contact potential difference associated with the difference in work function between probe and sample. In the terminology used in corrosion science, this measured quantity is commonly referred to as the Volta potential difference. SKPFM therefore combines the nanometre-scale topographical information of AFM with a map of local relative nobility across the surface.¹⁵⁸

The Kelvin technique is based on a nulling principle, in which an external bias (V_{CPD}) is applied to compensate the contact potential difference between probe and sample. If a Pt probe is used as reference, the measured Volta potential of the investigated metal may be written as

$$\psi_{Me} = \psi_{Pt} - V_{\text{CPD}} \quad (\text{tip biased}) \quad (2-42)$$

and

$$\psi_{Me} = \psi_{Pt} + V_{\text{CPD}} \quad (\text{sample biased}), \quad (2-43)$$

showing that the sign of the measured potential depends on whether the bias is applied to the tip or to the sample. For this reason, the magnitude and polarity of the applied bias must always be reported, since “high” and “low” potential values alone are insufficient for an unambiguous interpretation of local nobility.¹⁵⁸

For practical SKPFM measurements, the tip–sample distance is a particularly important parameter because the measured Volta potential depends strongly on separation distance. According to the review of Örnek et al., the potential follows a hyperbolic distance dependence and should ideally be measured at lift heights of about 50–100 nm; at distances below approximately 10 nm, surface-potential contributions and image-force effects become increasingly important, such that the measured quantity is no longer strictly the Volta potential.¹⁵⁸

An additional complication is that the measured Volta potential is extremely sensitive to surface condition and environment. Surface oxides, hydroxides, adsorbed species, humidity, temperature, sample preparation, and even changes in tip condition may alter the measured values substantially. For reliable interpretation, the tip should therefore be checked against a suitable reference sample, and SKPFM data should be reported together with the relevant experimental parameters, including surface finish, lift height, measurement mode, and bias polarity. Importantly, SKPFM does not measure the corrosion potential directly. It rather provides a local map of relative Volta potential that can be related to corrosion tendency only with appropriate caution and calibration.¹⁵⁸

In the context of the present work, AFM is primarily used to characterize nanoscale surface morphology, roughness, and local film coverage, whereas SKPFM complements this information by resolving local variations in relative surface nobility on modified metallic substrates. The combination of both methods is therefore particularly valuable for correlating topographical heterogeneity with local electrostatic surface properties of ultrathin corrosion-protective films.

2.4.3. Electrochemical characterization methods (fundamental concepts)

Electrochemical (EC) characterization methods are used to probe electrode processes under controlled electrical perturbation, thereby providing direct access to the thermodynamic tendency and, more importantly, to the rate of electrochemical reactions under non-equilibrium conditions. This section builds on the fundamentals introduced in Section 2.1.1, while additional concepts required for understanding the applied methods are presented in the respective sections. It begins with a brief introduction to the three-electrode configuration employed throughout this work. The individual methods are then described with respect to their fundamental principles and their specific relevance for the present thesis.

2.4.3.1. Three-electrode configuration

In electrochemical measurements, a potentiostat is usually employed. From a fundamental point of view, the potentiostat controls the potential of the working electrode (WE) and measures the current flowing between the working electrode and the counter electrode (CE).¹⁵⁹ A more detailed description of potentiostat operation can be found in Ref.¹⁶⁰.

The electrode arrangement used in this thesis is a three-electrode configuration, which represents the standard setup in conventional corrosion science. The WE is the electrode at

which the electrochemical processes of interest are investigated. The reference electrode (RE) provides a stable reference potential against which the potential of the WE is measured. Ideally, no current should pass through the RE, since this would disturb its potential and compromise the accuracy of the measurement. For this reason, a third electrode, the CE, is introduced to carry the current and thereby close the electrical circuit. The electrolyte serves as the ionic conductor between the electrodes and thus enables closure of the electrochemical circuit. At the same time, it defines the chemical environment of the measurement and may actively influence the investigated processes; in the presence of aggressive species such as chloride ions, it can also promote localized corrosion, as discussed in Section 2.1.3.1. Because the electrolyte has a finite resistance, the actual interfacial potential at the working electrode may deviate from the nominally applied potential due to ohmic potential drop.

2.4.3.2. LSV

The principle of linear sweep voltammetry (LSV) is the application of a linearly varying potential to the working electrode in either the anodic or cathodic direction. For this purpose, a defined starting potential is selected and then swept in one direction at a constant scan rate. LSV is a standard electrochemical method for investigating corrosion stability and corrosion-related processes on metal surfaces. The general procedure is usually as follows: first, the electrochemical system is allowed to equilibrate for a defined period of time. Depending on the aim of the study, this equilibration time may range from minutes to hours, and in some cases even up to days.⁴⁸ Second, the potential measured after the system has reached its quasi-stationary state is taken as the open-circuit potential (OCP). The linear sweep is then typically started at a cathodic potential relative to the OCP and scanned anodically until the final potential is reached. Evaluation of LSV data is usually done by extraction of kinetic parameters using the Tafel-plot and the Tafel equations (2-10) and (2-11), as discussed in Section 2.1.1.

2.4.3.3. Chronoamperometry

In chronoamperometry, the variation of the current response with time under potentiostatic control is investigated. Depending on the magnitude of the applied potential, the EC system can be studied in different circumstances, for example under mass-transport limitation.¹⁵⁹ In this thesis, a relatively small anodic potential step (100 mV) was applied to the working electrodes, hence the system should still be under activation control. Thus, the explained theoretics in Section 2.1.1 are applicable. However, by applying a potential step, the EC system is disturbed and strive to obey a new steady-state. This relaxation process is monitored by the current response of the system. An anodic step may also induce a more pronounced galvanic effect between the Al matrix and the intermetallic particles, making the alloy surface more prone to pitting corrosion. Thus, in this thesis CA is used as a qualitative or semi-quantitative method, to investigate corrosion susceptibility of the investigated Al alloy surfaces and the effect of applied surface modifications.

2.4.3.4. EIS

EIS is based on the analysis of the frequency-dependent impedance of an electrochemical interface. In this method, a small sinusoidal potential perturbation is applied to the working electrode over a defined frequency range, and the resulting sinusoidal current response is

recorded. In general, the current response is phase-shifted relative to the applied potential by the phase angle θ , which depends on the resistive and capacitive properties of the investigated system. The current amplitude is inversely proportional to the impedance of the interface.⁴⁹

The electrochemical impedance, $Z(\omega)$, is the frequency-dependent proportionality factor between the applied voltage signal and the measured current response and is given by

$$Z(\omega) = \frac{E(\omega)}{i(\omega)} \quad (2-44)$$

where E is the applied voltage, i is the resulting current density, and ω is the angular frequency. For a sinusoidal perturbation, the voltage and current signals may be written as $E = E_0 \cdot \sin(\omega t)$ and $i = i_0 \cdot \sin(\omega t + \theta)$, respectively. Since the current is generally phase-shifted relative to the voltage, impedance is described as a complex quantity. It can therefore be expressed either in terms of its modulus $|Z|$ and phase angle θ (also called “Bode-Plot”), or alternatively by its real and imaginary components, Z' and Z'' (also called “Nyquist-Plot”).⁴⁹ In this thesis, EIS data are visualized and discussed exclusively by Bode-Plots.

A common approach for interpreting EIS data is the use of equivalent circuit models, in which the electrochemical interface is represented by an electrical network of idealized circuit elements (see Figure 20B). In its simplest form, the metal/electrolyte interface can be described by three essential parameters: the electrolyte resistance R_{ely} , the double-layer capacitance C_{dl} and the polarization resistance R_p . The polarization resistance is sometimes also called the “charge-transfer resistance” R_{ct} . If the equivalent circuit model consists of R_{ely} in series with a parallel combination of C_{dl} and R_{ct} , it is referred to as a “Randles element”.

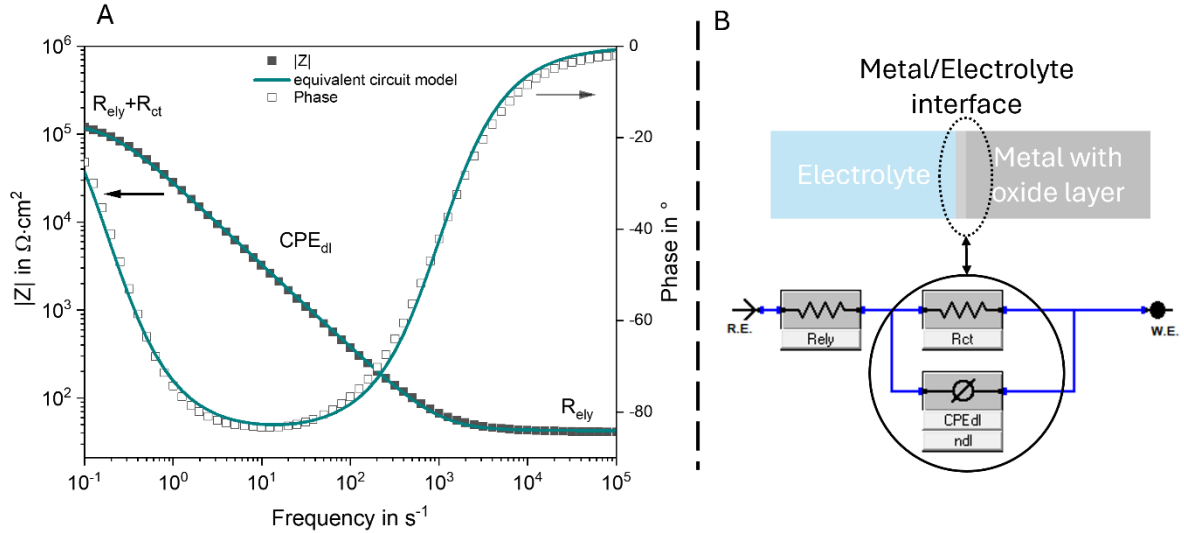


Figure 20. General Bode-Plot representation of EIS data with a fit of an equivalent circuit model inclusive a possible physical understanding of the electrode/electrolyte interface. In A, an EIS dataset of a polished and etched AlSi10Mg surface immersed in 0.1 M NaCl is shown. The data in A were modeled with the equivalent circuit shown in image B and the respective main circuit elements influencing $|Z|$ are given. In image B, the equivalent circuit used to model the data in A is shown. Additionally highlighted are the main equivalent circuit elements used to interpret EC processes at the metal/electrolyte interface during AC polarization.

As indicated in Figure 20A, under direct-current conditions, i.e. $\omega \rightarrow 0$, the impedance of the capacitive element approaches infinity. In the corresponding parallel branch, the current therefore passes predominantly through the resistive pathway, such that the measured resistance is given by the sum of R_s and R_{ct} . For $\omega \rightarrow \infty$ only the ohmic resistance of the electrolyte contributes to $|Z|$. Intermediate values for ω (usually between 10 and 100 s⁻¹) $|Z|$ is governed by capacitive processes. For non-ideal electrode surfaces, the capacitance of the EC system is usually exchanged by a constant-phase-element (“CPE”), accounting for the non-ideal capacitive behavior of the system.¹⁶¹ The impedance of a CPE is defined as

$$Z_{CPE} = \frac{1}{Q(j\omega)^n}, \quad (2-45)$$

where Q and n are independent of frequency and if n approaches 1, Q equals the unit of capacity.^{161,162}

To derive the effective capacitance (C_{eff}) from Q , the following equation can be used¹⁶³:

$$C_{eff} = Q_{CPE}^{\frac{1}{n}} \cdot (R_{ely})^{\frac{1-n}{n}}. \quad (2-46)$$

When mass transport or diffusion limitations become significant, the simple circuit model is often extended by an additional diffusion-related element, commonly denoted as the Warburg impedance Z_D .

In literature, the quality of EIS circuit fits are often described by the value χ^2 . The dimension of this parameter is usually around 10^{-3} .^{54,109} The following applies for that parameter: the smaller the value, the better the fit simulates the measured data.

2.4.4. Contact angle measurements

The wettability of metal surfaces plays an important role for corrosion susceptibility. The spreading of electrolyte on the metal surface is often associated with a higher corrosion tendency, especially when the surface has pores, cracks etc. In Section 2.1.4.3, the concept of wettability and the relationship between surface energies and the apparent contact angle θ by the Young-Dupré equation (2-18) have been introduced, but the phenomenon of surface tension or energy has not been discussed yet. Thus, this section first give a short definition of surface energies and surface tension and why it affects the wettability of surfaces. Afterwards, the concept of water contact angle measurements is introduced.

2.4.4.1. Relationship of surface tension, surface energy and contact angles

For a reversible increase in liquid surface area, work has to be done. The proportionality factor between the required work (ΔW) and the resulting surface increase (ΔA) is given by the following formula

$$\Delta W = \gamma \cdot \Delta A, \quad (2-47)$$

with γ denoting the surface tension in $\text{N} \cdot \text{m}^{-1}$. The terms surface tension and surface energy are often used interchangeably because, for liquids at equilibrium, they are numerically equivalent and both describe the energetic cost of creating a unit area of new surface.¹⁶⁴ In principle, this distinction could also be extended to solid surfaces. However, the determination of surface tension is considerably more complex for solids because, even in the simple case represented by eq. (2-5), the increase in surface area is governed not only by plastic but also by elastic contributions.¹⁶⁴ In addition, further influencing factors such as crystallographic phase and surface orientation have to be considered. Nevertheless, several approaches exist for estimating the surface energy of solids. One example is the so-called nearest-neighbor broken-bond model, which evaluates the energy required to break chemical bonds across a defined cross-sectional area. Other approaches are based on quantum-mechanical calculations. A further, indirect method relies on contact-angle measurements on low-energy solid surfaces. The equation describing the relation between contact angle and surface tensions, eq. (2-18), was already mentioned in Section 2.1.4.3. Rearrangement of this equation shows that the difference between the solid–gas and solid–liquid interfacial tensions is reflected in the contact angle of the probe liquid:

$$\gamma_{SG} - \gamma_{SL} = \gamma_{GL} \cdot \cos(\theta). \quad (2-48)$$

If $\gamma_{SG} > \gamma_{SL}$, the right side of eq.(2-48) is positive, so $\cos(\theta)$ has to be positive and the contact angle is smaller than 90° . In this case, the liquid is partially wetting the surface. If $\gamma_{SG} < \gamma_{SL}$, the contact angle will exceed 90° (also called “non-wetting”) because the solid-liquid interface is less energetically favorable.¹⁶⁴

It should be emphasized, however, that the relationship expressed by Young’s equation is strictly valid only for ideal solid surfaces. Such surfaces are assumed to be smooth, chemically homogeneous, rigid, insoluble in the probe liquid, and in thermodynamic equilibrium. Real engineering surfaces often deviate from these assumptions due to roughness, chemical heterogeneity, swelling, surface reconstruction, or adsorption processes. As a result, the experimentally measured contact angle frequently represents an apparent contact angle rather than an ideal Young contact angle. In addition, advancing and receding contact angles may differ, leading to contact angle hysteresis. Consequently, the interpretation of contact-angle data in terms of interfacial tensions and wetting behavior must be carried out with appropriate caution.

2.4.4.2. Static contact angles

Static contact-angle measurements are commonly performed using the sessile-drop method. In this approach, a droplet of defined volume is deposited onto the substrate surface and imaged from the side after allowing the drop to stabilize. The contact angle is obtained from the droplet profile at the three-phase contact line, either by tangent evaluation or by fitting the drop shape to an appropriate mathematical model (e.g. Laplace equation).¹⁶⁴ Because the measured angle depends on the local surface condition, parameters such as droplet volume, equilibration time, surface cleanliness, and ambient atmosphere must be controlled carefully to ensure reproducible results.

2.4.4.3. Dynamic contact angles

In dynamic contact-angle measurements, the wetting behavior of a liquid is characterized not by a single equilibrium angle, but by the advancing and receding contact angles. Experimentally, these angles are typically determined by increasing or decreasing the volume of a sessile drop while monitoring the motion of the three-phase contact line. Theoretically, the advancing contact angle is measured just before the wetting line starts to advance.¹⁶⁴ Practically, the advancing contact angle (θ_{adv}) is usually obtained when the contact line moves over previously dry surface, whereas the receding contact angle (θ_{rec}) is measured when the contact line withdraws from an already wetted area. The difference between both values is referred to as contact angle hysteresis (CAH) and provides important information on the interaction between the liquid and the real surface.¹⁶⁴

From a theoretical point of view, contact angle hysteresis arises because real surfaces are rarely ideally smooth and chemically homogeneous. Surface roughness, chemical heterogeneity, contamination, and adsorption of dissolved species can lead to pinning of the three-phase contact line and thereby hinder its motion.¹⁶⁴ During advancing, the contact line may be pinned by comparatively lyophobic regions, whereas during receding it may be pinned by more lyophilic regions. In addition, microscopic rearrangement of the wetting line often involves energy

dissipation, which further contributes to hysteresis. The magnitude of this effect depends not only on the chemical nature of the surface, but also on the length scale and geometry of surface features. Dynamic contact-angle measurements therefore provide more realistic information on wetting behavior than static measurements, particularly for structured or chemically heterogeneous surfaces.¹⁶⁴

3. Experimental

3.1. Substrate materials

The additively manufactured specimens were fabricated at the Chair of Material Science (Paderborn University) in the research group of Prof. Dr.-Ing. Mirko Schaper under the responsibility of Dr.-Ing. Kay-Peter Hoyer. In brief, gas-atomized AlSi10Mg powder (20-63 μm) supplied by Eckart TLS GmbH was used as the starting material. The particle size distribution (PSD) was determined by laser diffraction using a Mastersizer 3000 (Malvern Panalytical GmbH). Bulk density measurements were carried out as described in Ref.¹⁹ and yield a value of > 99.5 %.

Additive manufacturing was performed by LPBF using the as-received powder and an SLM 280HL machine (Nikon SLM Solutions AG, formerly SLM Solutions, Lübeck, Germany) equipped with a high-power laser. The applied process parameters correspond to conventional settings for AlSi10Mg and are listed in Table 2. Samples with dimensions of $10 \times 5 \times 10 \text{ mm}^3$ were fabricated in an argon atmosphere.

Following fabrication, the specimens were removed from the build platform by wire electrical discharge machining.

Table 2. LPBF process parameter for AM AlSi10Mg material used in this thesis. Adapted from Ref.¹¹⁵.

Laser source	Laser power, W	Scanning speed, mm/s	Scanning rotation, °	Layer thickness, μm	Volumetric energy density, J/mm^3
Ytterbium laser	365	1.650	67	50	34

EN AW 1050A alloy (> 99.5 wt%Al) has been purchased from Alumeco Deutschland GmbH. Polished and n-doped Si(100)-Wafer were obtained from Siegert Wafer GmbH (Germany). AW2024-T3 samples were obtained from GoodFellow Cambridge Ltd. (United Kingdom) with a producer stated composition of 93.5 wt%Al, 4.5 wt%Cu, 1.5 wt%Mg and 0.5 wt%Mn.

The Al alloy with a Cu content of 5.9 wt% (hereafter denoted as AlCu5.9) was produced at the Institute of Materials Science by Moritz Neuser. Alloy preparation was carried out by melting an Al-based feedstock (EN AW 1070) with copper in a crucible at 750 °C. After solidification, the material was solution heat treated at 530 °C for 3 h and subsequently quenched in water. The final composition, as determined by spark emission spectroscopy performed by Moritz Neuser, was approximately 93.9 wt% Al and 5.9 wt% Cu.

All materials were sectioned to the dimensions required for the respective investigations. In general, the specimens featured square surface areas between $10 \times 10 \text{ mm}^2$ and $20 \times 20 \text{ mm}^2$, with varying thicknesses depending on the intended analysis. As specimen geometry is not of central relevance to this thesis, further details are only provided where necessary.

Prior to the investigations, all specimens that had undergone any type of technical processing, such as sectioning or additive manufacturing, were cleaned using a three-step solvent cleaning procedure to remove lubricants and adhesive residues. First, the samples were treated in an ultrasonic bath (US, 45 kHz, 120 W, VWR International) in tetrahydrofuran (THF) for 10 min. This step was followed by ultrasonic cleaning in iso-propanol for 10 min and subsequently in absolute ethanol for 10 min. Further information on the chemicals used is given in Table 3.

3.2. Chemicals

An overview of all chemicals used throughout this thesis is provided in Table 3.

Table 3. Overview of the chemicals used throughout this thesis

Chemical	Supplier	Purity/Grade	Application
Tetrahydrofuran (THF)	VWR Chemicals Germany	p.A.	Solvent cleaning
Iso-propanol	VWR Chemicals Germany	p.A.	Solvent cleaning
Ethanol	VWR Chemicals Germany	99.8 %	Solvent cleaning, solvent for SAMs
PDMS oil (4.2 kDa)	ThermoFisher Scientific (Alfa Aesar)	97 %	Surface modification
Toluene	Sigma-Aldrich	99.8 %	Solvent cleaning
Methanol	Th. Geyer GmbH & Co. KG	99.85 % (for HPLC)	Spray-coating
Distilled water	VWR Chemicals Germany	For HPLC, $\leq 10^4 \Omega\text{m}$	Solvent cleaning
Doubly-distilled water (ultra-pure)	Carl Roth GmbH	$\geq 18 \cdot 10^6 \Omega\text{m}$	Solvent for electrolytes, solvent cleaning
ODPA	Sigma-Aldrich	97 %	SAM chemical
ODT	Sigma-Aldrich	98 %	SAM chemical
Ammonia (NH ₃ , 25%)	Stockmeier Chemie GmbH & Co. KG	98 %	SiO _x -CVD precursor
Tetraethoxysilane (TEOS)	ThermoFisher Scientific (Alfa Aesar)	98 %	SiO _x -CVD precursor
Sodium chloride (NaCl)	VWR Chemicals Germany	p.A.	Spray-coating, electrolyte
Boric acid (H ₃ BO ₄)	Merck KGaA	p.A.	Electrolyte (borate buffer)
Sodium sulfate (Na ₂ SO ₄)	Merck KGaA	p.A.	Electrolyte (borate buffer)
Sodium tetraborate decahydrate (Na ₂ B ₄ O ₇ · 10H ₂ O)	VWR Chemicals Germany	p.A.	Electrolyte (borate buffer)
Sodium hydroxide (NaOH, 2 wt%)	Merck KGaA	p.A.	Alkaline etchant
Nitric acid (HNO ₃ , 53 %)	Stockmeier Chemie GmbH & Co. KG	98 %	Acid etchant, desmutting
Aluminum oxide (Al ₂ O ₃)	Schmitz-Metallographie GmbH	0.3 μm particle size	Polishing agent

3.3. Surface technologies

This section provides an overview of the surface treatments and surface modification procedures applied throughout this thesis. The individual methods are described in terms of their experimental workflow and the respective processing parameters. Where necessary, brief information on the objective of the treatment is included to support the interpretation of the results discussed in the subsequent sections.

3.3.1. Mechanical and chemical surface pre-treatment

With the exception of most experiments conducted in the first study of this thesis, all specimens were subjected to a combined mechanical and chemical surface pre-treatment prior to further

investigation. For this, the samples were ground stepwise with SiC paper from 600 to 2500 grit and subsequently polished using a water-based 3 μm diamond suspension and a 0.3 μm $\alpha\text{-Al}_2\text{O}_3$ suspension. After polishing, residual polishing compounds were removed by ultrasonic cleaning in ethanol. The polished samples were then alkaline etched in 2 wt% NaOH for 30 s, rinsed with distilled water, and dried with purified air. Subsequently, desmutting was carried out in 53 % HNO_3 (Sigma-Aldrich) for 30 s, followed by rinsing with distilled water, washing with ethanol, and drying in a nitrogen stream.

The polished and etched specimens were subsequently used for further surface modification procedures or analytical investigations. If not processed immediately, the samples were stored until further use in a desiccator containing silica gel at a pressure of approximately 60 mbar.

3.3.2. O_2 -plasma cleaning

Unless otherwise stated, all AM AlSi10Mg specimens were subjected to O_2 -plasma treatment prior to further surface modification or analytical investigation. The treatment was carried out using a high-frequency plasma generator (Zepto B) from Diener electronic, which is shown in Figure 21. The specimens were placed on a clean glass slide and introduced into the plasma chamber. After sealing the chamber, the system was evacuated to approximately 0.1 mbar by means of a rotary vane pump. Once this pressure had been reached, oxygen was introduced via a needle valve until a total pressure of approximately 0.5 mbar was established. The plasma was ignited at 90 % generator power, corresponding to 90 W, and maintained for 30 s. During plasma operation, the total pressure increased slightly and remained between 0.5 and 0.6 mbar. After the treatment, the chamber was purged with oxygen for approximately 10 s, vented, and the pump was shut down. The specimens were then transferred to the subsequent treatment or analysis step without delay.



Figure 21. Photograph of the plasma generator used in this thesis. The left image shows the plasma chamber including the glass slide support for the samples. The right image shows the plasma generator with the O_2 gas flow and total pressure displays indicated.

3.3.3. SiO_x thin films by CVD

SiO_x thin films were deposited by a CVD process adapted from Teisala et al.⁴⁴ The samples were pretreated with O_2 -plasma. Subsequently, they were placed in a desiccator containing two quartz crystallization dishes filled with 25 % NH_3 and TEOS, respectively, and kept there for 4 h at

approximately 700 mbar. Unless stated otherwise, the samples were then subjected to a second O₂-plasma treatment.

3.3.4. UV-induced and room-temperature PDMS grafting

UV-induced PDMS grafting is adapted by Tesler et al.⁴⁶ Samples being selected for this grafting routine were previously treated with O₂-plasma and then fully covered with PDMS oil (approximately 100 µl). The covered samples are then exposed to UV light (OmniCure 1000) with a bandpass filter of 250–450 nm at a power density of approximately 50 mW/cm² for 30 minutes. After curing, the samples were subjected to sequential ultrasonic cleaning in toluene and ethanol for 10 minutes each. Subsequently, the samples were rinsed with doubly distilled water and ethanol. Finally, they were dried under a nitrogen stream and stored in a desiccator containing silica gel at a pressure of approximately 60 mbar for at least 1 h.

Room-temperature PDMS grafting is adapted by Teisala et al.⁴⁴ This grafting routine is also only applied to samples, which were previously treated with O₂-plasma. The samples were covered with approximately 100 µl PDMS oil and placed for 24 hours at atmospheric conditions. Following a reaction time of 24 h, the samples were subjected to sequential ultrasonic cleaning in toluene, ethanol and ultra-pure water for 10 minutes each. The samples were then rinsed with ethanol, dried under a nitrogen stream and stored in a desiccator containing silica gel at approximately 60 mbar for at least 1 h before further use.

3.3.5. SAM deposition

The specimens were immersed (if not otherwise noted) in 1 mM solutions containing either ODPA, ODT, or a combination of both compounds. Unless otherwise specified, the immersion time was 24 h. After treatment, the samples were rinsed with ethanol, dried under a nitrogen stream, and either directly subjected to analytical investigations or stored in a desiccator at approximately 60 mbar.

For AW2024 and AlCu5.9 samples, the Reference, i.e. the non-SAM treated sample, is immersed for 24 h in ethanol prior to any investigation, to provide accurate comparability with the SAM-coated samples.

3.3.6. Deposition of NaCl by spray-coating

Prior to NaCl deposition, the samples were weighed to determine their initial mass (m_{initial}) using a balance with a resolution of 10 µg. The samples were then mounted in sample holders specifically designed for the specimen dimensions of 15 × 15 mm². These holders featured a square opening of approximately 14 × 14 mm².

Subsequently, the spray solution was prepared as a NaCl-saturated methanolic solution and stirred for at least 10 min to establish saturation equilibrium. During this time, the samples were installed in a spray coater (ND-SP Spray Coater, Nadetech Innovations). The interior of the spray coater, including the parts and components required for the spraying process, is shown in Figure 22. The spray solution was then drawn into a syringe (25 ml) connected via a Luer-lock fitting to a tube (Masterflex), and any remaining air was removed. The syringe was mounted in the

designated holder equipped with a mechanical feed regulator, and the tube was connected to one of the spray nozzles. The feed regulator determined the volumetric flow rate delivered from the syringe.

The flow rate, as well as other parameters such as nozzle traverse speed, number of spray passes, and the distance between nozzle and sample, were optimized on the basis of preliminary test coatings, which were evaluated both visually and gravimetrically. In order to reproducibly achieve a NaCl surface loading of approximately $100\text{--}200\text{ }\mu\text{g cm}^2$ (exact values will be provided where appropriate), corresponding to values typical of coastal regions¹⁶⁵, a volumetric flow rate of $400\text{ mL}\cdot\text{h}^{-1}$ and a nozzle speed of $1000\text{ mm}\cdot\text{min}^{-1}$ was selected. Each sample were sprayed three times in consecutively steps. In addition, the nozzle was connected to an external gas supply to ensure sufficient atomization quality and spray pressure. Nitrogen was used as the carrier gas at a pressure of approximately three bar.

Before the spray process was started, the samples were heated to approximately $75 \pm 5\text{ }^\circ\text{C}$ using a heating plate located beneath the sample stage. Temperature control was achieved both externally via a testo 610 temperature sensor connected to a Pt100 element and internally via the spray coater software. Heating the samples to a temperature above the boiling point of methanol was essential to prevent spreading of the solvent and to obtain a homogeneous NaCl distribution. In addition, only one sample was coated at a time in order to avoid possible re-deposition of spray mist on neighboring substrates.

After completion of the spray process, the chamber was exhausted using an extraction system connected to a laboratory fume hood. The sample was then removed from the holder, and the procedure was repeated for the remaining specimens. After coating, the samples were weighed again to determine their mass after NaCl deposition (m_{NaCl}). The NaCl surface loading was calculated by dividing the mass difference between m_{NaCl} and m_{initial} by the coated surface area.

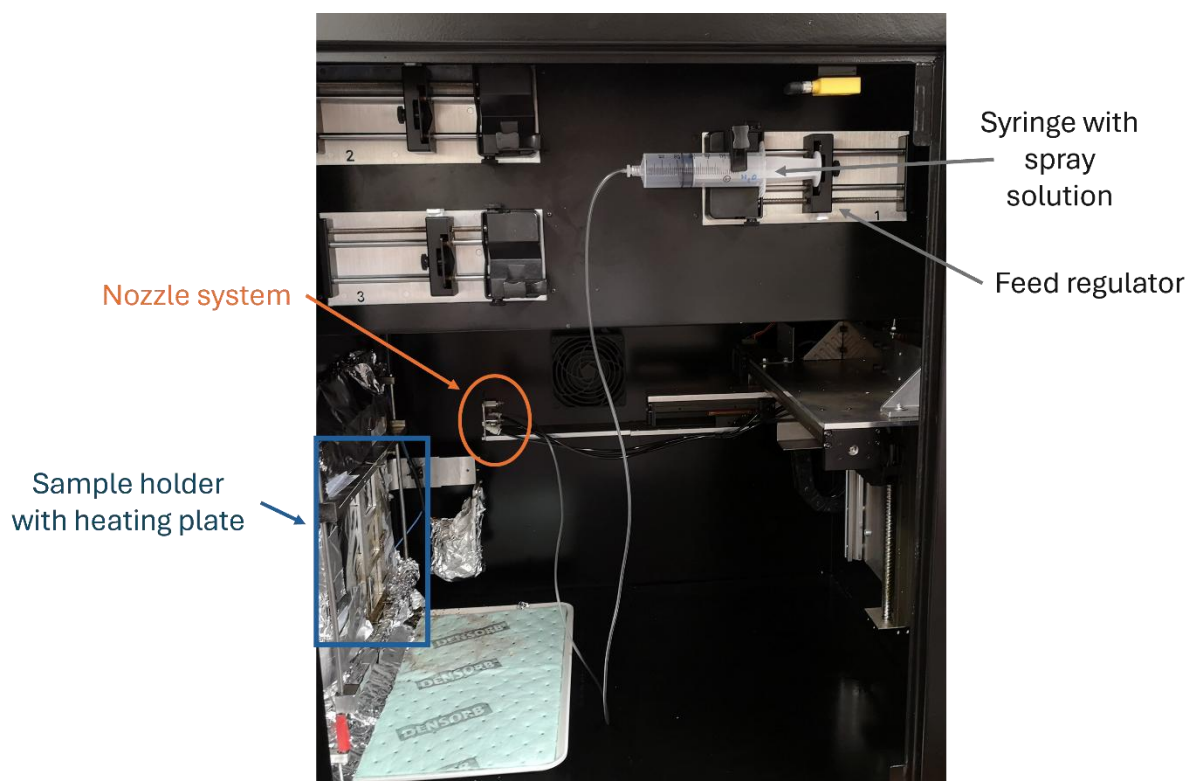


Figure 22. Interior view of the ND-SP Spray Coater (Nadetech Innovations). The syringe and feed regulator system, the sample holder with heating plate, and the nozzle system are highlighted.

3.4. Atmospheric corrosion exposure cells

Two different exposure cells were employed in this thesis. The first cell was designed for long-term exposure experiments and did not allow operando microscopic observations. The second cell was used for the investigation of shorter exposure periods by digital microscopy. Both cell types are described in detail in the present section.

3.4.1. Long-term exposure cell

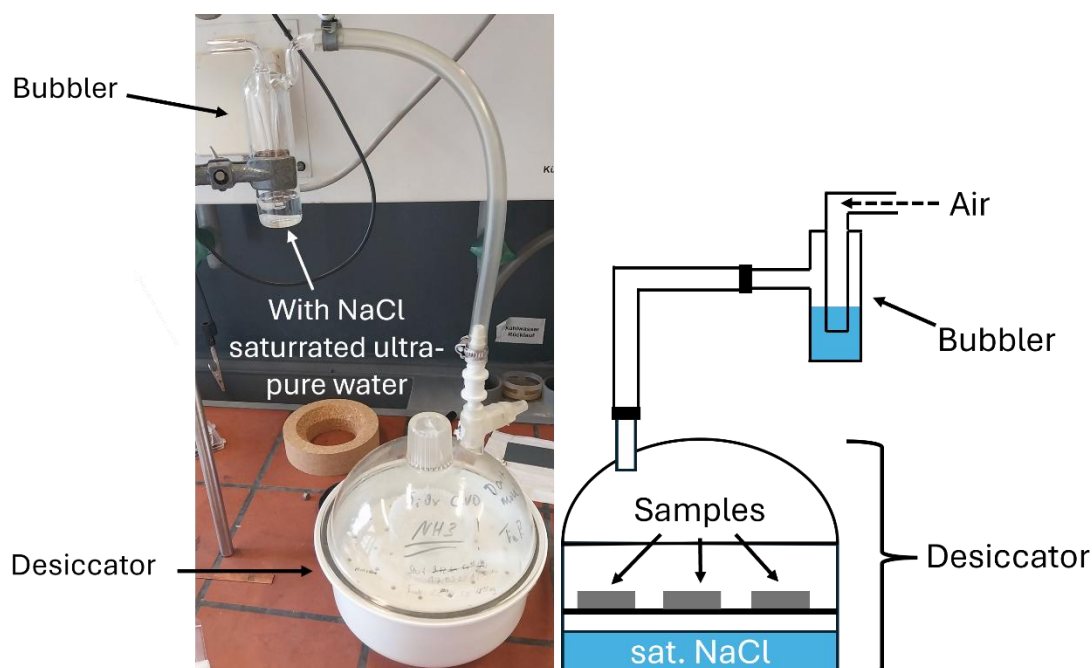


Figure 23. Experimental setup of the long-term atmospheric exposure cell. The left image shows a photograph of the cell system, and the right image shows a schematic representation of the experimental setup for clarity.

The cell shown in Figure 23 consisted of a desiccator connected via tubing to a bubbler. Both the desiccator and the bubbler were filled with an aqueous saturated NaCl solution. The specimens subjected to atmospheric exposure were placed on a ceramic plate positioned above the NaCl solution. Since the deliquescence point of NaCl is approximately 75 %r.h., a corresponding humidity level was expected to establish above the saturated NaCl solution. This was confirmed over several days using a humidity sensor (SHT4x SmartGadget, Sensirion). Over a period of 4 days, an average relative humidity of 75 ± 2 % was measured. The temperature, recorded with the same sensor, was 20.5 ± 1 °C.

To maintain stable pressure and gas composition during extended exposure periods, the desiccator was connected to a bubbler likewise filled with saturated NaCl solution. This arrangement ensured that ambient air entering the desiccator was humidified before contact with the samples.

3.4.2. Short-term exposure cell

The short-term exposure cell consisted of a screw-fastened airtight housing sealed with an attached transparent microscope glass slide. The cell was equipped with two ports for gas inlet and outlet. In addition, a small amount of adhesive putty (Blue Tack®) was applied between the gas inlet and outlet openings to keep the sample in position. A photograph of this cell, including its main components and the humid air flow path, is shown in Figure 24. With this setup, the cell could be mounted beneath the digital microscope used in this thesis, allowing in operando observation of droplet formation and corrosion processes.

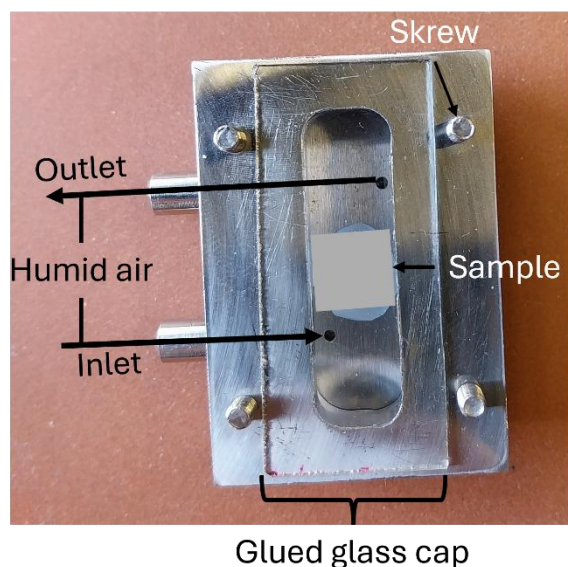


Figure 24. Cell used for short-term atmospheric exposure investigations. The cell was sealed airtight using screws. The sample was positioned between the gas inlet and outlet openings. The top of the cell consisted of a bonded transparent microscope glass slide, allowing visual observation by microscopy.

For this setup, a more humid gas stream than that used in the long-term exposure cell was deliberately selected in order to accelerate wetting and corrosion reactions. The humidified air stream was generated using a custom-built humidification system. As this setup was not constructed by the author, only a brief description of its general design is provided here.

At the inlet of the humidification system, a purified air stream was divided into a humid and a dry branch. The flow rates of both streams were measured and adjusted by means of flow controllers according to the desired target humidity. The humid branch was passed through three temperature-controllable gas washing bottles filled with water and connected in series. The heated humid air stream was subsequently brought to 25 °C in a thermostatic bath and then combined with the dry air stream. Before entering the cell, the humidity of the mixed gas stream was monitored using a humidity sensor. The target humidity was set to 90 %r.h., with an average deviation of approximately 2 %r.h.

The experimental setup that produced the image shown in Figure 48 (Section 4.3.1) was assisted by Yinuo He.

3.5. Surface investigation methods

3.5.1. Digital microscopy

Digital microscopic observations were performed using a VHX-7000 digital microscope (Keyence). The system provides optical imaging with integrated 2D/3D measurement capabilities, large depth of field, and multi-angle observation. In this work, magnifications of up to 500x were applied.

For 3D imaging, the microscope acquires images at different focal planes along the z-axis. These images are combined by the software to generate a fully focused image and to reconstruct the surface topography from the associated height information. R_a values are calculated from eq. (2-38).

3.5.2. FE-SEM and EDS

FE-SEM was used to characterize the surface topography of the investigated samples. Micrographs at various magnifications were recorded with a NEON 40 FE-SEM instrument (Carl Zeiss SMT AG) equipped with InLens and SE2 detectors. Electron acceleration voltages ranged from 2-4 kV. The detector and electron acceleration voltage used for each image is given in the respective Figure caption (i.e. Figure 29 Figure 37 and Figure 49). Elemental identification was carried out by EDS using the same instrument. Measurements were performed at an acceleration voltage of 4 kV for AlSi10Mg samples and 10 kV for AlCu5.9 alloy. In every case, the aperture size was 60 μm . An UltraDry detector (Thermo Fisher Scientific Inc.) was used for EDS analysis. FE-SEM/EDS analyses were performed by Nadine Buitkamp.

3.5.3. Water Contact angle measurements

Static water contact angle measurements were carried out using an OCA 15 plus system (Dataphysics) at room temperature (approximately 20 °C). For each measurement, 5 μL water droplets were dispensed onto the respective surface by means of a motor-driven syringe system. The droplet contours were fitted according to the Laplace equation, and the corresponding contact angles were determined. For each surface condition, at least three samples were evaluated, with one to four measurements conducted per sample.

The experimental setup for dynamic contact angle measurements was slightly modified. While the OCA 15 plus system was still used, the measurements were performed under elevated humidity to avoid droplet volume changes caused by evaporation during the measurement. To establish this atmosphere, the sample was covered with a crystallizing dish whose edges were lined with water-soaked soft cotton. An opening was introduced into the side of the dish facing the syringe unit of the contact angle instrument to allow access of the syringe to the sample. Using this setup, a constant relative humidity above 90 % was maintained. Under these conditions, the water droplet retained its shape and volume for at least 30 min, which exceeded the time required for a single measurement.

For each dynamic contact angle measurement, an initial droplet volume of 10 μL was deposited onto the respective surface. The syringe needle was then positioned in the center of the droplet. Subsequently, 4 μL was added to determine the advancing contact angle, followed by the withdrawal of 4 μL to determine the receding contact angle. The dosing speed was 0.5 $\mu\text{L}\cdot\text{s}^{-1}$. Contact angles were evaluated as described for the static measurements. This procedure was repeated at least five times. During addition and withdrawal, care was taken to ensure that the droplet diameter increased and decreased, respectively, in order to obtain the physically correct advancing and receding contact angles.

3.5.4. PM-IRRAS

PM-IRRAS was used to characterize the sample surfaces after each modification step. Measurements were performed with a Bruker Vertex 70 spectrometer (Bruker Optics, Germany). The angle between the detector and the surface normal of the samples was fixed at 80° . Infrared beam polarization was achieved using an aluminum wire-grid polarizer and modulated at 50 kHz by means of a ZnSe photoelastic modulator (PMA50, Bruker, Germany). A photograph of the PM-IRRAS assembly, showing the main components and the path of the IR laser, is shown in Figure 25. To compensate for the wavelength-dependent optical throughput and detector response of the PMA50 setup, spectra were acquired in two separate measurements, with the optical focus adjusted to approximately 3000 cm^{-1} and 1500 cm^{-1} , respectively, in order to maximize the signal-to-noise ratio in both the C-H stretching and fingerprint regions. The reflected light from the substrates was focused onto a cryogenic mercury cadmium telluride (MCT) detector using a ZnSe lens. All modified samples were measured using 512 scans, a spectral resolution of 4 cm^{-1} , and a mirror speed of 10 kHz. An aperture between 1.0 and 1.5 mm was used to maximize signal intensity while avoiding detector overload. A photograph of the experimental setup is shown in Figure 25, including the indicated IR beam path and the identification of the key components. Data processing was carried out with OPUS 7.8 software (Bruker Optics, Germany), applying a polynomial background correction to all spectra in a consistent manner in order to remove the background contribution of the Bessel function.¹⁶⁶

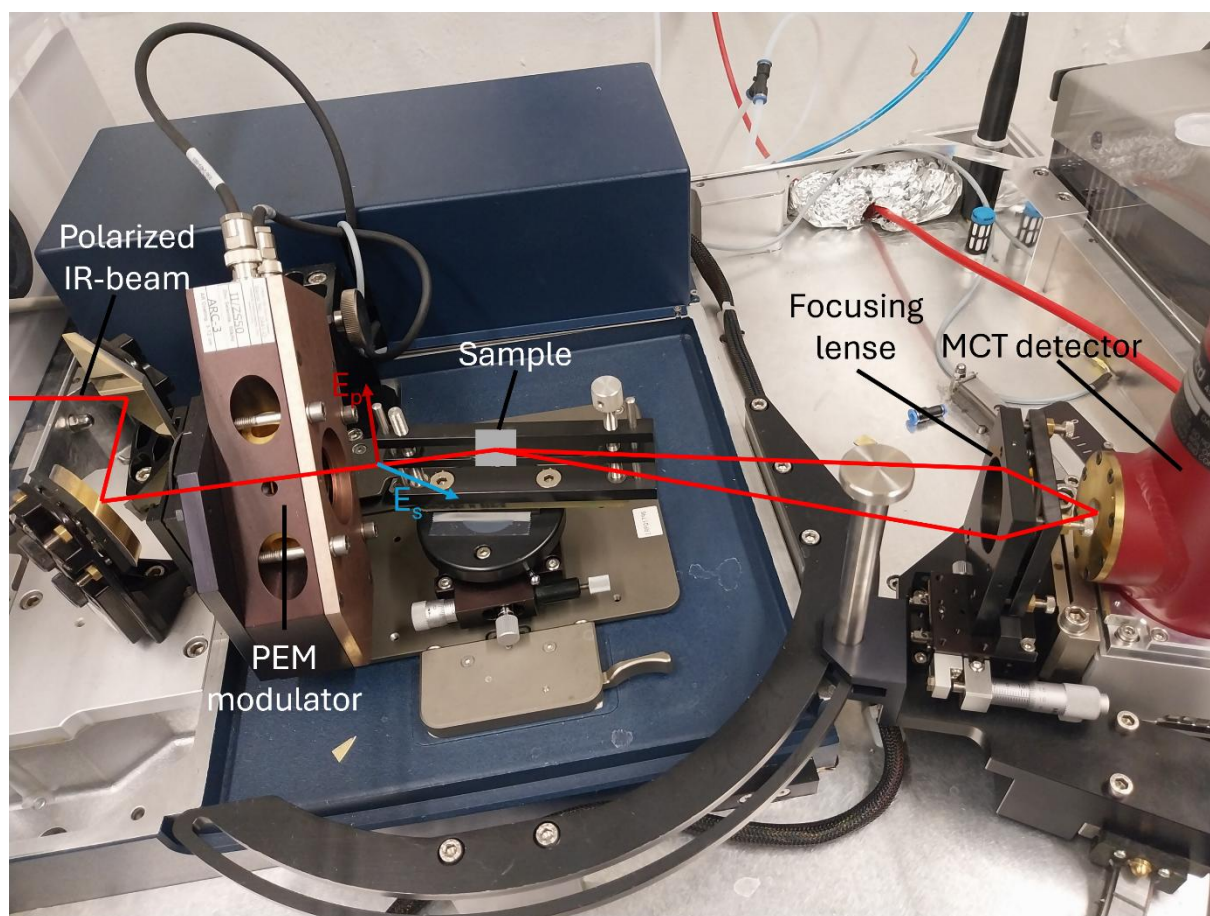


Figure 25. PM-IRRAS setup used in this thesis. Shown are the polarized IR beam, the photoelastic modulator (PEM), the electric field vectors parallel and perpendicular to the plane of incidence (E_p and E_s , respectively), the sample surface, the focusing lens, and the MCT detector.

3.5.5. XPS

X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical composition of the cleaned and modified surfaces. Measurements were carried out using an Omicron ESCA+UHV system (Scienta Omicron NanoTechnology GmbH, Germany) equipped with a monochromated Al K α X-ray source (1486.3 eV). The effective analyzed surface area was approximately 3.1 mm². All measurements were recorded at a base pressure below 4×10^{-10} mbar. Photoelectrons were detected using an analyzer positioned at an angle of 30° relative to the sample surface plane, while the angle between the X-ray source and the detector was 102°.

For each modified specimen, two survey spectra were acquired in the range from 0 to 1350 eV using a step size of 0.5 eV and a pass energy of 100 eV. These spectra were (if not otherwise noted) used for elemental quantification. Atomic compositions were evaluated in CASA XPS software (CASA Software Ltd.) after background subtraction using a Shirley function for O1s, C1s, Si2p, and Al2p, and a linear background for F1s and N1s. Quantification was based on the software-integrated relative sensitivity factors (RSFs), with effective values of 2.93, 1.00, 0.69, 0.45, 4.43, and 1.8, respectively.

In addition, high-resolution spectra of the Si2p and Al2p regions were recorded with a pass energy of 20 eV, a step size of 0.1 eV, and a dwell time of 0.5 s. Under these conditions, the full width at half maximum (FWHM) of the Ag3d5/2 peak at 368.1 eV, measured on a freshly sputtered Ag reference sample, was 0.77 eV. All spectral components were fitted using a GL(30) line shape, corresponding to a convolution of 70% Gaussian and 30% Lorentzian character. The metallic Si(0) and Al(0) contributions in the Si2p and Al2p spectra were fitted using an asymmetric Gaussian/Lorentzian product function, A(a,b,n)GL(30), where a and b describe the asymmetry and n defines the width of the Gaussian used to convolute the basic peak shape.¹⁶⁷ A Shirley background was applied in all cases.¹⁶⁸

3.5.6. ToF-SIMS

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) depth profiling was performed at the Interdisciplinary Center for Analytics on the Nanoscale (ICAN) of the University of Duisburg-Essen using a TOF.SIMS 5 instrument (IONTOF). The analysis beam was generated by a liquid metal ion gun (LMIG) operated in delayed extraction and random raster mode with Bi⁺ primary ions at 30 kV. Measurements were carried out in negative ion polarity over an analysis area of 100 × 100 μm^2 with 256 × 256 pixels. Sputtering was performed in non-interlaced mode using Cs⁺ ions at 500 V over an area of 400 × 400 μm^2 . No charge compensation was applied during the measurements, i.e., both the flood gun and O₂ gas flooding were switched off.

Secondary ion signals considered for the evaluation included H⁻, C⁻, CH⁻, O⁻, C₂H⁻, Al⁻, P⁻, S⁻, HS⁻, ³⁴S⁻, C₃H⁻, AlO⁻, PO⁻, SO⁻, C₄H⁻, Al₂⁻, AlO₂⁻, Cu⁻, CuO⁻, Al₃⁻, Al₂O₃⁻, Al₄⁻, Al₂Cu⁻, Cu₂⁻, Al₅⁻, AlCu₂⁻, Al₆⁻, Al₂Cu₂⁻, and Cu₃⁻. In addition, summed ion intensities were used to characterize specific chemical contributions, including sulfur-containing species (S⁻, HS⁻, ³⁴S⁻, SO⁻), phosphorus-containing species (P⁻, PO⁻), hydrocarbons (CH⁻, C₂H⁻, C₃H⁻, C₄H⁻), the bulk Al phase (Al₂⁻, Al₃⁻, Al₄⁻, Al₅⁻, Al₆⁻), the bulk Al₂Cu phase (Cu₂⁻, AlCu₂⁻, Al₂Cu₂⁻, Cu₃⁻), and aluminum oxide (AlO⁻, AlO₂⁻, Al₂O₃⁻). Additional sulfur- and phosphorus-containing mass peaks were not considered because of significant mass interferences.

To obtain an estimate of the sputter rate, the depth of the final ToF-SIMS sputter crater was measured by confocal profilometry using an S neox 090 instrument (Sensofar) equipped with a 20× brightfield objective. Measurements were carried out over an area of $845 \times 707 \mu\text{m}^2$ with a resolution of 2448×2048 pixels using green LED illumination. For this purpose, the etched Al/Al₂Cu sample treated in ODPa solution, was selected, as the comparatively long sputter time of 1218 s resulted in the deepest crater.

The average sputter rate was estimated from the crater depth and the corresponding sputter time. Due to the pronounced surface topography and waviness of the sample, the depth determination was subject to considerable uncertainty, and measured crater depths ranged from approximately 40 to 130 nm. Consequently, only a rough estimate of the average sputter rate could be obtained, yielding a value of approximately $0.07 \text{ nm} \cdot \text{s}^{-1}$. Based on this average value, the first 25 s of sputtering correspond to an estimated depth of about 2 nm. It should be noted, however, that sputter rates depend strongly on the material, and the value given here represents only an average estimate. In particular, sputter rates of organic coatings are typically higher than those of oxides and metallic phases.

To account for differences in the region of interest (ROI) size and phase fraction between the individual samples, ROI-specific calibration factors were used for the comparison of the phase-resolved ion intensities. These calibration factors are given in Table 4.

Table 4. Regions of interest (ROI) defined for the Al-rich and Cu-rich (denoted as Al₂Cu) areas of the investigated samples and the corresponding calibration factors applied for phase-specific evaluation of the ToF-SIMS data. In each case, the total image size was 65536 pixel.

Surface state	Size / Calibration factor Al ₂ Cu-ROI	Size / Calibration factor Al-ROI
Reference	4182 pixel / 15.67	53109 pixel / 1.24
ODPA	6078 pixel / 10.78	50885 pixel / 1.29
ODT	2620 pixel / 25.01	51861 pixel / 1.26
ODPA+ODT	1872 pixel / 35.01	57505 pixel / 1.14

ToF-SIMS experiments have been executed and analyzed by Prof. Dr. Nils Hartmann, at the Interdisciplinary Center for Analytics on the Nanoscale (ICAN) of the University of Duisburg-Essen

3.5.7. AFM and SKPFM

AFM and SKPFM measurements discussed in this thesis were carried out using a Dimension Icon system (Bruker). An SCM-PIT-V2 cantilever (Bruker) with a PtIr-coated tip was used. The cantilever has a nominal resonance frequency of 75 kHz and a nominal spring constant of $3 \text{ N} \cdot \text{m}^{-1}$. The drive frequency used for imaging was approximately 57.5 kHz. SKPFM measurements were performed

in interleaved lift mode, with a lift height of approximately 54 nm. Typical scans were recorded over an area of $5 \times 5 \mu\text{m}^2$ with 512×512 pixels at a scan rate of approximately 0.45 Hz. No additional DC bias was applied to either the sample or the tip during the measurements. The metadata suggest that an AC excitation of 5.0 V at 1.953 kHz was used during the KPFM pass. In order to assess the relative nobility of the tip, a reference measurement was carried out on a well-defined test sample (PFKPFM-SMPL, Bruker). The sample consists of a Si wafer featuring defined Au and Al domains with known surface potential contrast. For this measurement, the same cantilever was used as for the measurements performed on the polished and etched AlSi10Mg alloy. The result of the reference measurement is shown in Figure S1 in the Supporting Information. AFM/SKPFM data visualization was performed using Gwyddion software (version 2.61). No image or data processing was applied to the reference measurement or to any of the SKPFM measurements. The height data of the AlSi10Mg surfaces were leveled by subtraction of the mean plane.

3.5.8. Electrochemical investigations

This section provides an overview of the electrochemical droplet cell used in this work as well as the measurement parameters applied for electrochemical characterization.

3.5.8.1. *Electrochemical droplet cell*

Electrochemical measurements were carried out using a droplet cell integrated into the OCA 15 Plus system, which was likewise used for water contact angle measurements. The used glass capillary had an inner diameter of 2.4 mm and an outer diameter of 3.0 mm. The droplet cell was operated in a three-electrode configuration, with the sample serving as the working electrode. A gold counter electrode and an Ag/AgCl (3 M KCl) reference electrode were used. Figure 26 shows a schematic diagram of the droplet cell and a photograph of the experimental setup.

The integrated camera system of the contact angle instrument enabled visual observation of the electrolyte contact with the sample surface. This allowed the exposed electrode area to be adjusted to $0.07 \pm 0.01 \text{ cm}^2$. The selected area was verified in spot checks using the image analysis software ImageJ and was visually adjusted for each individual measurement based on the outer diameter of the capillary. Furthermore, for polished samples exhibiting salt residues after electrochemical testing, digital microscopic images were acquired and the electrode area was evaluated where possible. Thus, this setup enabled precise positioning of the capillary relative to the sample surface without direct mechanical contact, thus avoiding damage to the thin films and suppressing crevice corrosion.

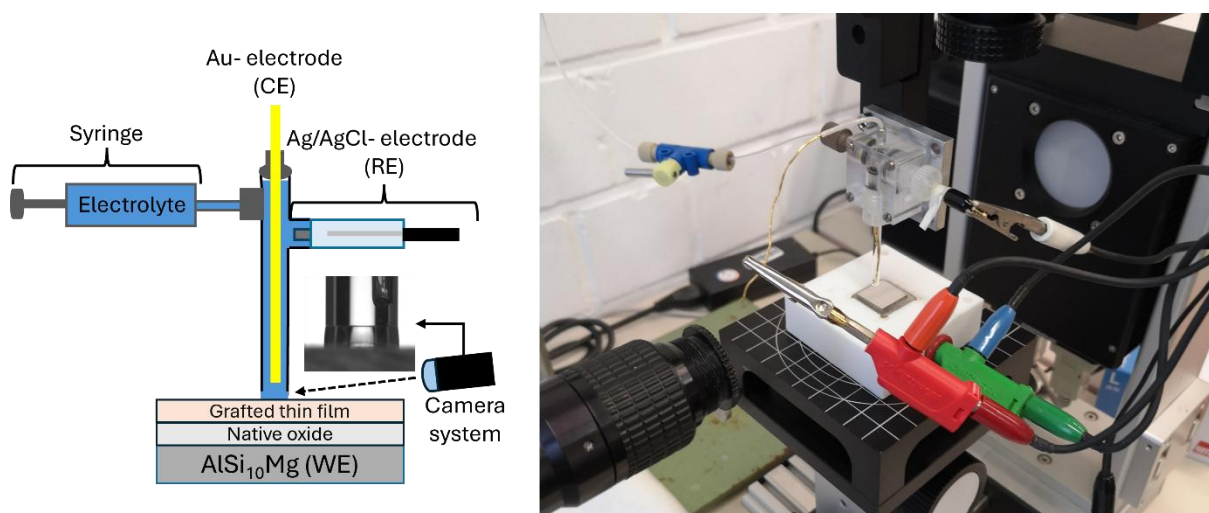


Figure 26. Experimental setup of the droplet cell used for electrochemical measurements in this thesis. The left image shows a schematic illustration of the droplet cell and its components, and the right image shows a photograph of the experimental setup. The cell comprised a glass capillary filled with electrolyte via a connected syringe, a gold wire serving as the counter electrode, and an Ag/AgCl reference electrode (3 M KCl). Electrolyte contact with the Al sample, acting as the working electrode, was monitored using the camera system of the OCA 15 Plus instrument.

3.5.8.2. Electrochemical analysis

Before polarization measurements were performed, OCP was monitored for at least 300 s. The last recorded OCP value was subsequently taken as the basis for the following electrochemical measurements.

Electrochemical impedance spectroscopy (EIS) was performed with an AC excitation voltage of either 10 mV (for as-produced AlSi10Mg surfaces) or 20 mV (all polished surfaces) in the frequency range between 100 kHz and 0.1 Hz. All recorded EIS spectra were evaluated for consistency by applying a Kramers–Kronig (K–K) test within the Gamry software package.¹⁶⁹ The Gamry software package was also employed to generate equivalent circuit models and fit them to the EIS data in order to gain further insight into the investigated electrochemical system.

Linear sweep voltammetry (LSV) measurements were carried out by applying a potential sweep from -0.15 V vs. OCP to +0.5 V vs. OCP at a scan rate of 2 mV s⁻¹. These datasets were used for Tafel analysis as described in Section 2.4.3.2. Anodic LSV measurements were performed by sweeping the potential from OCP to +0.7 V vs. OCP at a scan rate of 2 mV s⁻¹. Chronoamperometry was used to examine the relaxation behavior of the electrochemical system for the individual surface states. For this purpose, a potential of 0.1 V vs. OCP was applied for a maximum duration of 800 s.

LSV measurements for AW2024 substrates were carried out by applying a potential sweep from -0.15 V vs. OCP to +0.4 V vs. OCP at a scan rate of 5 mV s⁻¹.

Used electrolyte for as-produced AlSi10Mg surfaces was a borate buffer solution, containing 0.2 mol L⁻¹ H₃BO₄, 0.05 mol L⁻¹ Na₂SO₄, 0.05 mol L⁻¹ Na₂B₇·10 H₂O and 0.05 M NaCl in ultra-pure water.

Other used electrolytes were either composed of unbuffered 0.1 M NaCl (used in Section 4.2.5) or 0.1 M Na₂SO₄ (used in Section 4.3.4).

4. Results and Discussion

This section presents and discusses the experimental results obtained within the three main studies of this thesis. In order to maintain a clear structure, the results are divided into separate sections corresponding to the individual subprojects. Although each section focuses on a distinct material condition and surface modification strategy, all parts are connected by the overarching objective of this work: the development and evaluation of nanoscale coating concepts for chemically and microstructurally heterogeneous aluminum alloys.

The central aim is to understand how molecular, polymeric, and inorganic thin-film systems interact with heterogeneous alloy surfaces and how these interactions affect surface chemistry, wettability, electrochemical activity, and corrosion protection. Particular emphasis is placed on the relationship between local microstructure, interfacial film formation, and functional corrosion-inhibiting performance. The section therefore follows a structure–chemistry–function approach, in which morphological and chemical surface characteristics are first correlated with the formation of nanoscale interphases and subsequently linked to electrochemical and corrosion-related behavior.

The results are organized into three main sections. Section 4.1 addresses the sequential functionalization of as-built additively manufactured AlSi10Mg surfaces by PDMS grafting and subsequent ODPa adsorption. The results of this study have been partially published in Ref.¹¹⁵. Section 4.2 focuses on polished and chemically etched AlSi10Mg surfaces and compares direct PDMS grafting with a combined SiO_x/PDMS coating architecture. The results of this study have been partially published in Ref.¹⁷⁰. Section 4.3 extends the concept of chemically selective surface functionalization to Al–Cu-based systems by investigating the adsorption of self-assembled molecules on chemically heterogeneous phases of AW2024-T3 and a model AlCu alloy.

4.1. Molecular functionalization of as-built AM AlSi10Mg surfaces by PDMS and ODPa

4.1.1. Scope and research question

This section investigates whether nanoscale molecular and polymeric surface modifications can be applied directly to as-built additively manufactured AlSi10Mg surfaces. This surface state is of particular interest because it combines high technological relevance with pronounced topographical and chemical heterogeneity, which is expected to complicate homogeneous thin-film formation.

PDMS grafting and ODPa adsorption were selected as complementary modification strategies. While PDMS is expected to form a hydrophobic polymeric interphase on the rough AM surface, ODPa, as a low-molecular-weight adsorbate, may occupy residual surface sites that remain inaccessible or ungrafted after PDMS modification. In addition, the chemical heterogeneity of the surface is expected to influence molecular adsorption preferences. Their sequential combination therefore provides a model system to evaluate whether chemically distinct surface domains of

AM AlSi10Mg can be addressed more effectively by a combined modification strategy than by a single surface chemistry.

The following sections examine the relationship between as-built surface morphology, chemical film formation, wetting behavior, and electrochemical barrier properties. In doing so, this part of the thesis addresses how the local heterogeneity of AM AlSi10Mg governs the formation and protective function of nanoscale organic interphases. For a better understanding, Figure 27 summarizes the experimental approach of this study.

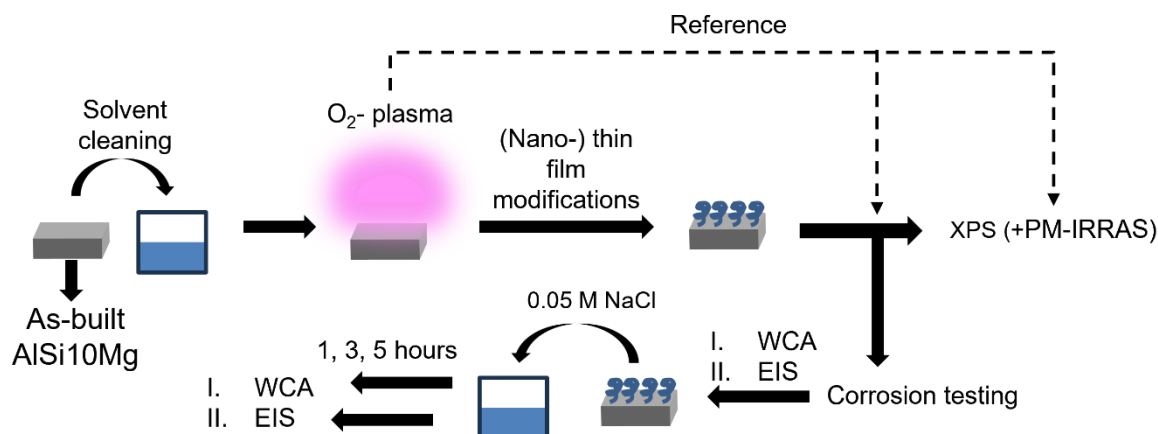


Figure 27. Experimental approach used to investigate PDMS and ODPA surface modifications on as-built AM AlSi10Mg surfaces. The AlSi10Mg specimens were solvent-cleaned and, unless otherwise stated, activated by O_2 -plasma treatment. The samples were then left unmodified as reference surfaces or modified by ODPA adsorption, PDMS grafting, or sequential PDMS+ODPA treatment. The resulting surface states were either analyzed spectroscopically or exposed to 0.05 M NaCl solution for defined immersion intervals. WCA and EIS measurements were performed before exposure and repeated ex situ after each immersion interval. Adapted from Ref.¹¹⁵.

4.1.2. Surface morphology and chemical heterogeneity of as-built AM AlSi10Mg

The morphology and chemical composition of the as-built AlSi10Mg surface define the initial boundary conditions for all subsequent surface modification steps. In contrast to mechanically polished substrates, the as-built surface does not provide a smooth and chemically uniform oxide surface. Instead, it reflects the characteristic process history of laser powder bed fusion, including local melting and solidification, partial remelting of adjacent powder particles, oxidation during processing, and the formation of rough topographical features.

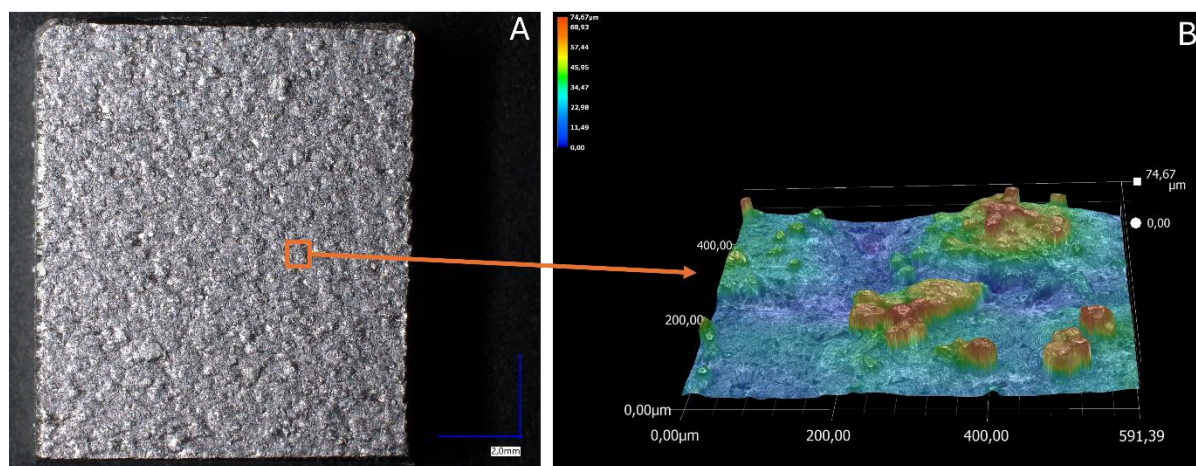


Figure 28. Digital microscopic analysis of the as-built AM AlSi10Mg surface morphology. Image A shows a stitched overview image reconstructed from multiple digital micrographs acquired under different illumination conditions. Image B shows a three-dimensional height map of a representative $600 \times 600 \mu\text{m}^2$ area, illustrating the pronounced topographical heterogeneity of the as-built surface.

Digital microscopy was used to evaluate the topographical heterogeneity of the as-built AM AlSi10Mg surface. As shown in Figure 28A, the stitched overview image reveals an irregular surface morphology typical of the as-manufactured state. The corresponding 3D height map in Figure 28B further confirms pronounced local height variations within a representative $600 \times 600 \mu\text{m}^2$ area. From line profile analysis extracted from the 3D height data (Figure S2) R_a values of $14.2 \pm 7.1 \mu\text{m}$ has been calculated. This value underline the pronounced roughness of the as-built surface and indicate that the substrate does not provide a planar interface for nanoscale film formation. Such topographical features are relevant for the subsequent surface functionalization, as they may affect wetting behavior, local electrolyte retention, and the formation of homogeneous PDMS or ODPA layers.

FE-SEM analysis further confirms the pronounced morphological heterogeneity of the as-built AM AlSi10Mg surface. As shown in Figure 29A, the surface is characterized by irregular topographical features, attached unmelted or partially molten powder particles, and particle agglomerates (indicated by blue arrows). At higher magnification, Figure 29B reveals local surface defects, protruding structures, and regions with distinct surface textures. These features indicate that the surface morphology varies substantially on the micrometer scale. The high-magnification image in Figure 29C additionally shows nanoscale particle-covered areas adjacent to comparatively smooth regions. Although the chemical nature of these particles cannot be assigned unambiguously from FE-SEM alone, their local distribution demonstrates that the as-built surface is heterogeneous down to the nanometer scale. Such multiscale heterogeneity is expected to affect the uniformity of subsequent PDMS grafting and ODPA adsorption and may provide preferential pathways for electrolyte retention or penetration.

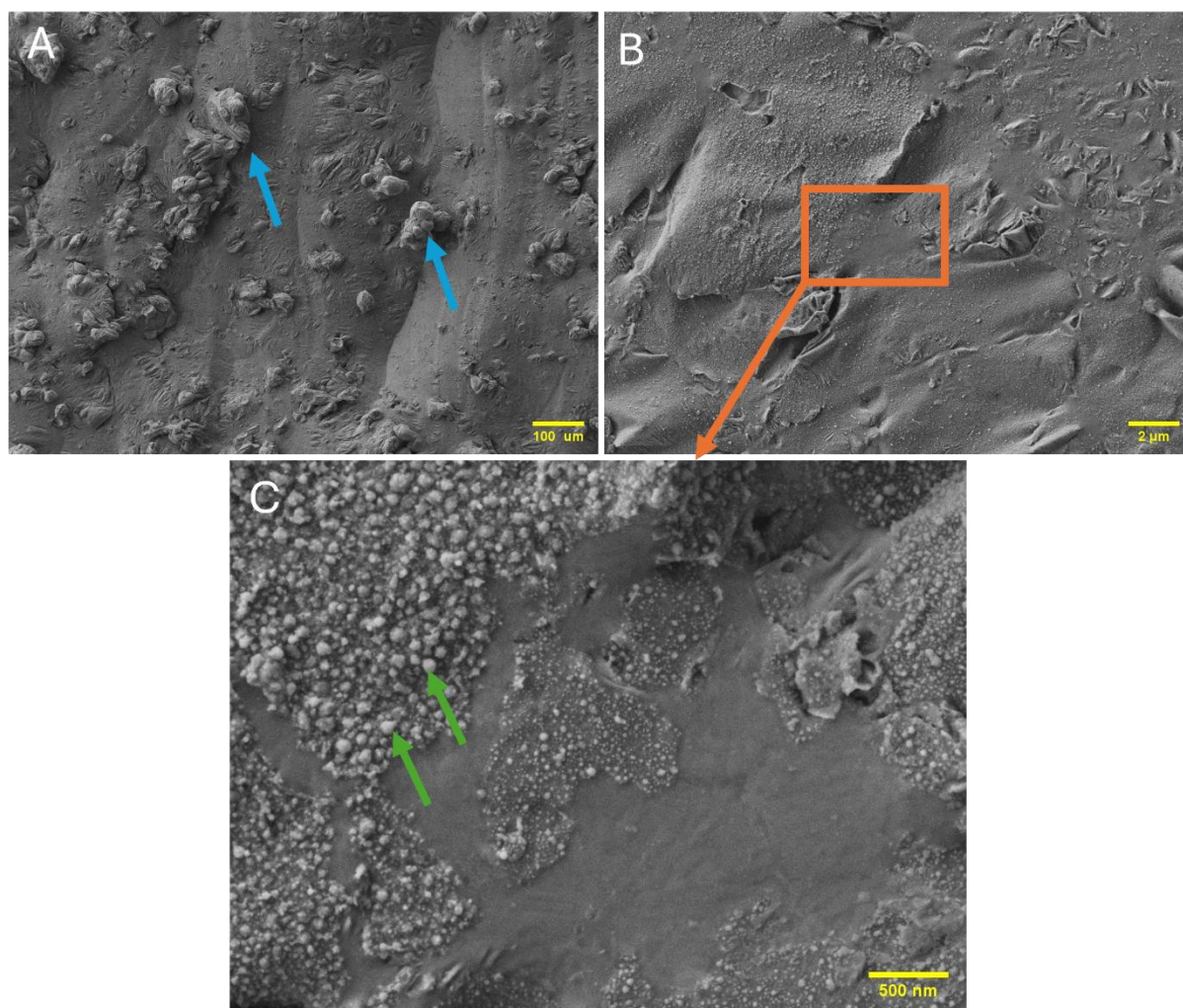


Figure 29. FE-SEM images of the O_2 -plasma-treated as-built AM AlSi10Mg surface at different magnifications. The images were recorded with the SE2 detector. Electron acceleration voltage for each image was 2 kV. Image A shows a low-magnification overview image showing the pronounced topographical heterogeneity of the as-built surface, including attached unmelted or partially molten powder particles and particle agglomerates, indicated by blue arrows. Image B shows a higher-magnification image revealing local surface defects, protruding structures, and regions with different surface textures. The highlighted area marks the position shown in higher detail in image C. Image C shows a high-magnification image showing nanoscale particle-covered regions adjacent to comparatively smooth surface areas. The nanoscale particles indicate an additional level of surface heterogeneity, although their chemical composition cannot be assigned from FE-SEM imaging alone.

The chemical heterogeneity of the as-built surface was further investigated by EDS mapping. As shown in Figure 30, the Al K signal is detected over the entire analyzed region, reflecting the aluminum-rich matrix of the alloy. In contrast, the Si K map reveals local variations in silicon distribution, which are consistent with the heterogeneous Al–Si phase distribution generated during LPBF processing. The O K signal is likewise not uniformly distributed but appears locally enhanced at topographically pronounced surface features, indicating oxidized surface regions or oxide-rich process-related structures. The Mg K signal is comparatively weak, as expected from the low Mg content of AlSi10Mg, and does not allow an unambiguous assignment of specific Mg-containing particles in this representation. Due to the pronounced roughness of the as-built surface, the EDX maps should be interpreted as semi-quantitative indicators of local elemental distribution rather than as strictly quantitative surface composition data. Nevertheless, the results clearly demonstrate that the surface provides chemically distinct Al-, Si-, and O-

containing regions, which are expected to influence the subsequent PDMS grafting and ODPA adsorption behavior.

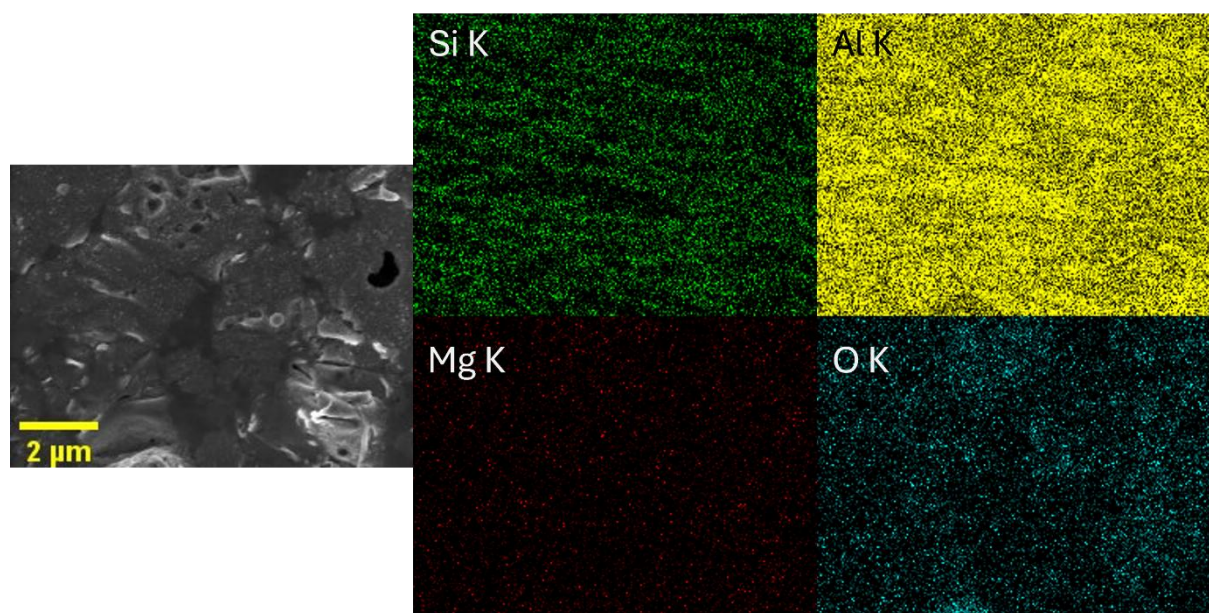


Figure 30. EDS analysis of the as-built AM AlSi10Mg surface after O_2 -plasma activation. The grey-scale image shows the corresponding FE-SEM micrograph of the surface region selected for EDS mapping. The elemental maps display the spatial distribution of the Al K, Si K, Mg K, and O K signals. The Al signal is distributed across the entire investigated area, whereas the Si and O maps reveal local variations associated with the chemically heterogeneous Al–Si surface and oxidized surface features. The Mg signal is comparatively weak and locally distributed. The color scales represent semi-quantitative atomic percentages obtained from the EDX analysis. Adapted from Ref.¹¹⁵.

Taken together, the digital microscopic, FE-SEM, and EDS results demonstrate that the as-built AM AlSi10Mg surface is characterized by pronounced multiscale topographical roughness and local chemical heterogeneity. These features define a non-ideal and spatially variable interface for nanoscale film formation and therefore provide the basis for the following chemical analysis of PDMS grafting, ODPA adsorption, and their sequential combination.

4.1.3. Interfacial chemistry and wettability of PDMS- and ODPA-modified surfaces

In the next step, the as-built AM AlSi10Mg surface was modified by PDMS grafting, ODPA adsorption, and sequential PDMS+ODPA treatment. The resulting surface states were first characterized by XPS in order to assess the chemical composition and subsequently analyzed by means of high-resolution spectra of C1s and Si2p elements. These results were subsequently correlated with water contact angle measurements to evaluate the modification-induced changes in surface wettability.

Table 5. Elemental quantification from XPS survey spectra of the investigated as-built AM AlSi10Mg surface states. Values are reported as mean atomic concentrations $\pm$ standard deviation based on 2–4 samples or measurement positions per surface condition. “Reference (no O₂-plasma)” was measured once and is therefore listed without standard deviation. Representative survey spectra are provided in Figure S3 in the Supporting Information.

Core level	Reference (no O ₂ - plasma)	Reference	ODPA _{24h}	PDMS _{grafted}	PDMS _{grafted} +ODPA _{24h}
O1s	39.3	50.3 $\pm$ 0.5	33.5 $\pm$ 0.3	38.1 $\pm$ 3.7	30.1 $\pm$ 2.9
C1s	29.5	8.4 $\pm$ 1.2	33.8 $\pm$ 1.8	23.3 $\pm$ 4.9	40.4 $\pm$ 5.3
Mg1s	1.3	1.8 $\pm$ 0.5	0.4 $\pm$ 0.2	0.3 $\pm$ 0.3	-
Al2p	22.4	30.3 $\pm$ 2.3	21.9 $\pm$ 1.1	22.3 $\pm$ 4.4	19.1 $\pm$ 2.9
Si2p	3.0	5.3 $\pm$ 2.3	4.3 $\pm$ 0.9	13.9 $\pm$ 3.5	7.9 $\pm$ 0.5
P2s	-	-	1.5 $\pm$ 0.2	-	1.2 $\pm$ 0.5
F1s	0.4	1.9 $\pm$ 0.4	2.9 $\pm$ 2.5	1.3 $\pm$ 1.5	0.5 $\pm$ 0.6
Na1s	-	0.2 $\pm$ 0.2	-	-	-
Ca2p	1.5	1.1 $\pm$ 0.2	1.6 $\pm$ 1.0	0.8 $\pm$ 0.2	0.8 $\pm$ 0.1
S2p	1.7	-	-	-	-
N1s	1.2	0.6 $\pm$ 0.2	-	-	-

XPS survey analysis was used to evaluate the chemical composition of the as-built AM AlSi10Mg surface before and after O₂-plasma activation and subsequent surface modification. The results are summarized in Table 5 and individual XP survey spectra are shown in Figure S3. The non-plasma-treated Reference surface shows a comparatively high C1s contribution of 29.5 at%, indicating the presence of organic surface contamination or adventitious carbon (AdC). After O₂-plasma treatment, the C1s concentration decreases markedly to 8.4 at%, while the O1s and Al2p contributions increase from 39.3 at% and 22.4 at% to 50.3 at% and 30.3 at%, respectively. This confirms the effective removal of carbonaceous surface species and the exposure of an oxidized Al-rich surface. The O₂plasma-treated Reference surface is therefore dominated by oxygen and aluminum signals, while the detected Si2p contribution of 5.3 at% reflects silicon-containing surface domains associated with the AlSi10Mg alloy, which is alignment with EDS results in

Figure 30. However, it should be emphasized that due to the pronounced roughness and chemical heterogeneity of the as-built surface, the XPS quantification should be interpreted as an area-averaged and semi-quantitative representation of the outermost surface composition.

After ODPA adsorption, the surface composition changes markedly. The C1s concentration increases to 33.8 at%, while a distinct P2s signal of 1.5 at% appears. The simultaneous increase in carbon and phosphorus is consistent with the adsorption of ODPA on the oxidized AlSi10Mg surface. At the same time, the O1s and Al2p contributions decrease to 33.5 at% and 21.9 at%, respectively. This attenuation of substrate- and oxide-related signals indicates the formation of an organic overlayer. The experimentally obtained C/P ratio is higher than the nominal stoichiometric ratio of ODPA, which can be attributed to contributions from adventitious carbon, the roughness of the as-built surface, and the semi-quantitative nature of XPS analysis on topographically heterogeneous substrates.

For the PDMS-modified surface, the most pronounced change is the increase in the Si2p contribution from 5.3 at% for the reference surface to 13.9 at%. Together with the increase in C1s intensity to 23.3 at%, this confirms the successful grafting of a PDMS-derived surface layer. The increase in Si content is consistent with the siloxane backbone of PDMS, while the corresponding carbon signal arises mainly from the methyl groups bound to silicon. The measured C/Si ratio is lower than the ideal stoichiometric ratio of PDMS. This deviation is reasonable because the detected Si2p signal contains contributions from both the PDMS layer and the silicon-containing alloy surface. In addition, UV-induced modification of the PDMS structure may contribute to a partial loss of methyl groups during grafting.⁴⁶

The sequential PDMS+ODPA modification leads to the highest C1s concentration of all investigated surface states, with 40.4 at%. In addition, a P2s signal of 1.2 at% is detected, confirming that ODPA is present after adsorption onto the PDMS-pretreated surface. However, the Si2p contribution decreases from 13.9 at% after PDMS grafting to 7.9 at% after subsequent ODPA adsorption. This decrease is considerably higher than the decrease of Al2p, which decreases of about 3 at%. Sections 4.1.4 and 4.1.5 experimentally investigate whether this supposedly significant loss of the Si2p signal can be explained by attenuation effects or whether interfacial reorganization might be proposed as a possible explanation.

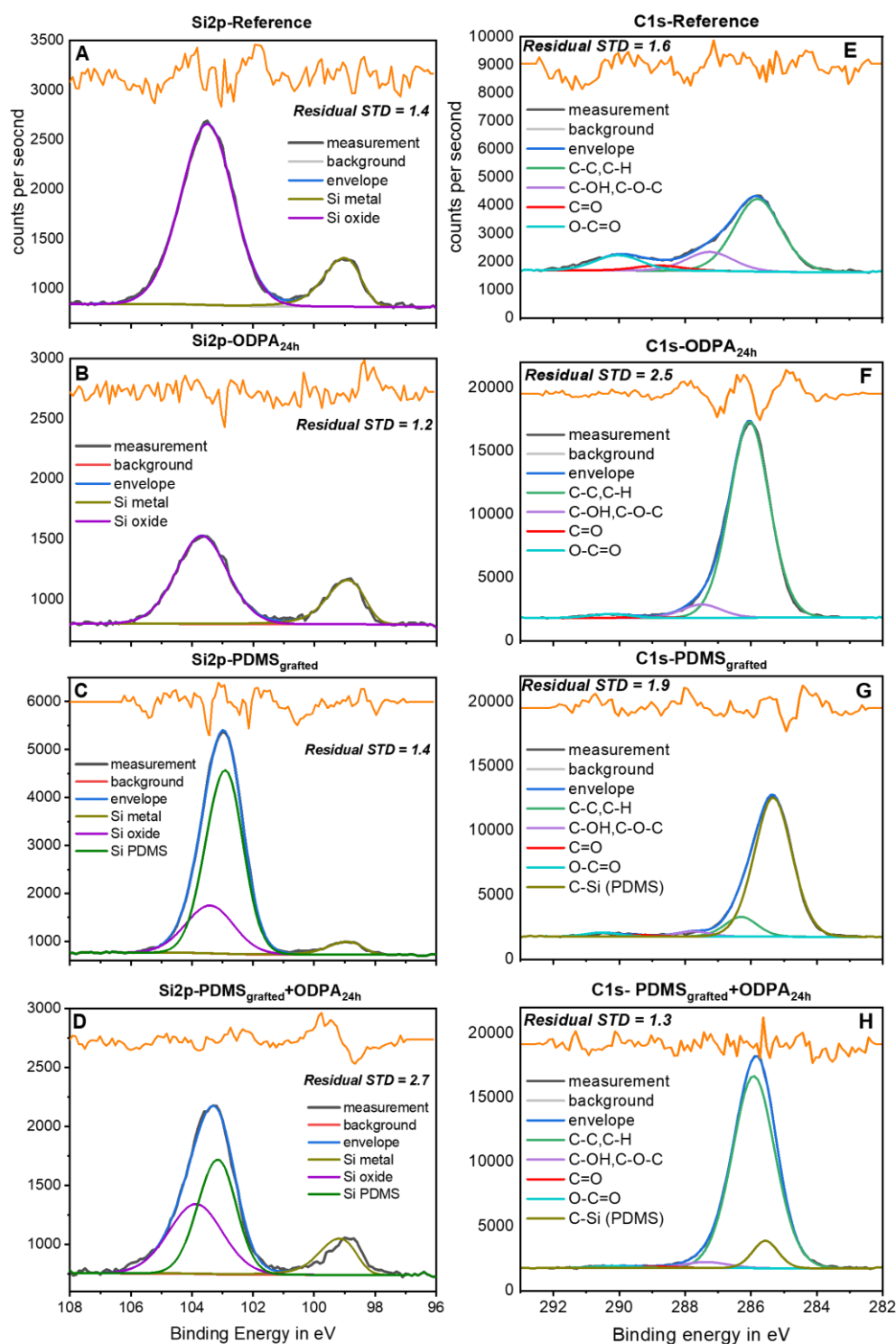


Figure 31. High-resolution-XPS component fits of the Si2p and C1s narrow scans recorded for the modified and non-modified AM AlSi10Mg surfaces. The Si2p spectra are shown for (A) the O₂-plasma-cleaned reference surface, (B) the ODPA-modified surface, (C) the PDMS-modified surface, and (D) the PDMS+ODPA-modified surface. The corresponding C1s spectra are shown in (E–H) in the same order. The residual standard deviations (residual STD) of the applied fits relative to the measured data are included in each spectrum. The ordinates are not scaled equally for improved clarity. Reproduced from: Prüßner et al. (2026) “Surface functionalization of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting”, *Materials Chemistry and Physics*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ Minor changes were made.

To obtain more detailed information on the chemical composition of each surface modification, high-resolution XPS spectra of the Si2p and C1s regions were evaluated (Figure 31; fitting parameters are summarized in Table S1 in the Supporting Information). For the Si2p spectra, spin-orbit splitting was considered according to the NIST database^{171,172}, and component fits belonging to the same chemical species are displayed as combined contributions for clarity. The binding energies assigned to metallic Si and native silicon oxide are in good agreement with reported literature values.^{96,173}

After PDMS grafting, the oxidized Si contribution increased markedly, consistent with the presence of a PDMS-derived siloxane layer. Therefore, an additional component assigned to PDMS-related silicon species ("C-Si(PDMS)") was introduced into the Si2p fit. Although this contribution is not clearly resolved as a separate peak in the Si2p envelope, its inclusion is chemically reasonable because the presence of PDMS is independently supported by the C1s spectra, and later shown results from PM-IRRAS, WCA and EIS. To avoid overparameterization of the fit, the fitting parameters of the native silicon oxide contribution were constrained using the corresponding Reference states. For the PDMS-modified sample, the parameters obtained from the Reference surface were used, whereas for the PDMS+ODPA surface, the parameters derived from the ODPA-modified surface were applied. The Si-PDMS contribution was assumed to occur at lower binding energy than the native silicon oxide contribution, consistent with the decrease in binding energy after PDMS grafting (compare Table S1). Based on this fitting approach, the relative Si2p contribution assigned to Si-PDMS decreased from 72.4 % for the PDMS-grafted surface to 48.3 % after 24 h of ODPA adsorption.

A corresponding component analysis was performed for the C1s spectra. For the unmodified Reference surface, the C1s envelope was fitted using typical AdC contributions according to Biesinger.¹⁷⁴ The ODPA-modified surface was fitted using the same general approach, but with a dominant C-C/C-H contribution, as expected from the long aliphatic chain of ODPA. Residual carbon-containing species were assigned to standard AdC components and constrained relative to the main C-C/C-H contribution.

After PDMS grafting, the main C1s peak shifted by approximately 0.7 eV toward lower binding energy compared with the ODPA-modified surface, which is due to the lower BE of C-Si in contrast to C-C/C-H components.^{175,176} The component analysis confirms this assignment: the C-Si contribution accounts for 68.0 % of the total C1s signal for the PDMS-grafted surface. After subsequent ODPA adsorption for 24 h, this contribution decreases strongly to 7.5 %, while the aliphatic C-C/C-H contribution becomes dominant.

The HR-XPS results therefore support the trends observed in the XPS survey quantification. In particular, the pronounced decrease of both the Si-PDMS contribution in the Si2p region and the C-Si contribution in the C1s region indicates that ODPA adsorption on PDMS-grafted AlSi10Mg does not merely result in the deposition of an additional molecular overlayer. Instead, the data point toward a partial reorganization or removal of PDMS-related surface species during ODPA adsorption. This finding provides the first spectroscopic indication of a competitive adsorption or exchange process, which is discussed in more detail in the following section.

In the next step, the effect of surface modification on water wettability is shown and discussed. In Table 6 the water contact angles of the different surface states are shown.

Table 6. Water contact angle values of different surface states of as-built AM AlSi10Mg substrates. Values are reported as mean $\pm$ standard deviation.

Measured value	Reference (no plasma)	Reference	ODPA _{24h}	PDMS _{grafted}	PDMS _{grafted} +ODPA _{24h}
Water contact angle	27.3 $\pm$ 3.2 °	Below detection limit (< 10 °)	136 $\pm$ 1.7 °	129.6 $\pm$ 2.2 °	134.4 $\pm$ 1.8 °

The non-plasma-treated as-built surface exhibits a water contact angle of 27.3 °, indicating a hydrophilic surface state even before plasma activation. After O₂-plasma treatment, the water contact angle decreases below the detection limit of the measurement setup (< 10 °), as the water droplet spreads almost immediately on the activated surface. This behavior is consistent with the XPS results, which show a pronounced reduction of carbonaceous surface species and an increased contribution of oxide-related surface signals after plasma treatment. The O₂-plasma-treated reference surface can therefore be described as a highly polar and strongly hydrophilic surface state.

In contrast, all organic surface modifications lead to a pronounced increase in water contact angle. ODPA adsorption results in a contact angle of 136.0 °, confirming the formation of a low-surface-energy interface dominated by outward-oriented alkyl chains. PDMS grafting likewise strongly increases the water contact angle to 129.6 °, which is consistent with the presence of methyl-terminated PDMS species at the outer surface. The sequential PDMS+ODPA modification yields a similarly high contact angle of 134.4 °, demonstrating that the combined treatment also produces a strongly hydrophobic surface. These values show that both ODPA and PDMS efficiently transform the initially hydrophilic, O₂-plasma-activated AM AlSi10Mg surface into a water-repellent interface. The magnitude of measured WCA values align well with literature values.^{44,46,177}

Together with the XPS survey quantification and HR-XPS component analysis, the WCA results confirm the successful formation of organic surface modifications on the as-built AM AlSi10Mg surface. While XPS provides evidence for ODPA-, PDMS-, and PDMS+ODPA-derived species in the outermost surface region, the contact angle measurements demonstrate the functional consequence of these modifications, namely a strong reduction in surface wettability. It should be noted, however, that the measured contact angles represent apparent values on a rough as-built surface. Therefore, they confirm the formation of a hydrophobic outer interface but do not by themselves prove the formation of a homogeneous or defect-free nanofilm.

4.1.4. Time-dependent ODPA adsorption and interfacial reorganization on PDMS-pretreated surfaces

After confirming the successful formation of the individual and combined surface states, the ODPA adsorption on PDMS-pretreated AM AlSi10Mg surfaces was investigated in more detail. The central question of this section is whether ODPA simply forms an additional molecular layer on top of the PDMS-modified surface or whether the adsorption process induces a partial reorganization of the pre-existing PDMS-derived interphase. For this purpose, PDMS-grafted as-

built AM AlSi10Mg surfaces were exposed to ethanolic ODPA solution for different adsorption times. In addition, a PDMS-grafted sample immersed in pure ethanol was analyzed as a control in order to distinguish between ODPA-induced and solvent-induced changes. The time dependency was ex-situ investigated by XPS. The results are summarized in Figure 32.

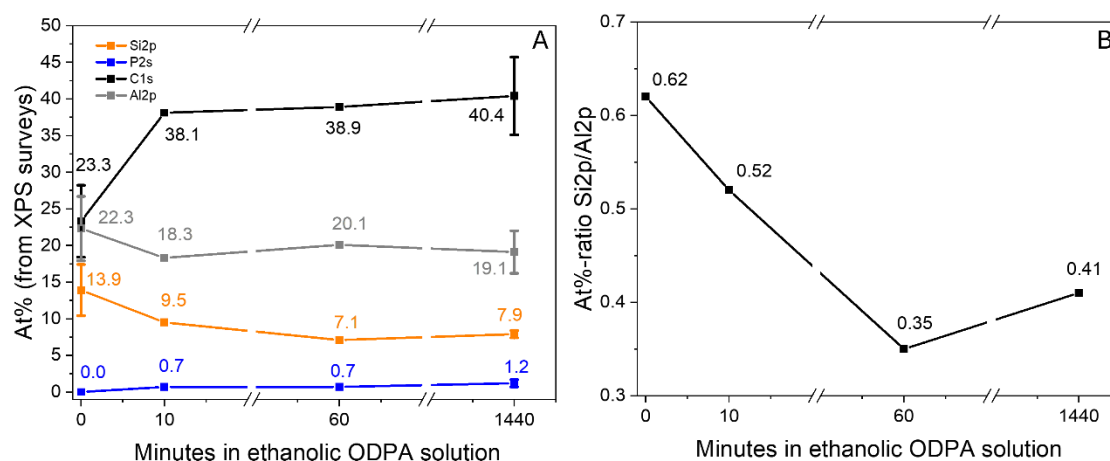


Figure 32. Time-dependent XPS analysis of ODPA adsorption on PDMS-grafted as-built AM AlSi10Mg surfaces. In image A, the elemental contributions of Si2p, Al2p, C1s, and P2s derived from XPS survey spectra as a function of ODPA adsorption time. Image B shows the corresponding Si2p/Al2p ratio, illustrating the relative decrease of silicon-containing surface species compared with the aluminum-related substrate signal during ODPA adsorption.

Figure 32A shows that after PDMS grafting, the surface exhibits a pronounced Si2p contribution of 13.9 at%, which is assigned to the PDMS-derived siloxane layer together with substrate-related silicon contributions (see Section 4.1.3). No P2s signal is detected in this state, confirming the absence of ODPA before exposure to the phosphonic acid solution.

Already after 10 min of immersion in ethanolic ODPA solution, a P2s contribution of 0.7 at% appears, indicating rapid adsorption of ODPA-derived species. Simultaneously, the C1s contribution increases, consistent with the introduction of the long alkyl chains of ODPA. Most importantly, the Si2p signal decreases markedly from 13.9 at% to 9.5 at% within this first adsorption interval. With longer adsorption times, the P2s contribution remains detectable and increases to 1.2 at% after 24 h, while the Si2p contribution remains at 7.9 at%.

The increase in P2s and C1s confirms the adsorption of ODPA-derived species on the PDMS-grafted surface. At the same time, the Si2p/Al2p ratio decreases from approximately 0.62 for the PDMS-grafted surface to 0.52 after 10 min of ODPA adsorption and further to approximately 0.35–0.41 after longer adsorption times, as reflected in Figure 32B. This observation indicates that the silicon-containing surface contribution is reduced more strongly than the aluminum-related contribution during ODPA adsorption. Although attenuation by a newly adsorbed ODPA overlayer may contribute to the observed decrease in Si2p intensity, the relative decrease of Si2p with respect to Al2p suggests that a simple overlayer model is not sufficient to describe the compositional changes, with respect to eq.(2-31). Instead, the data indicate that ODPA adsorption is accompanied by a partial alteration or reorganization of the PDMS-derived interphase.

An ethanol control experiment further supports this interpretation. Exposure of a PDMS-grafted surface to pure ethanol does not affect the Si2p contribution and does not lead to the appearance of a P2s signal. Thus, solvent exposure cannot explain the pronounced decrease in Si2p observed in the presence of ODPa. The stronger compositional change during ODPa adsorption therefore indicates that ODPa actively participates in the reorganization of the PDMS-modified interface.

Taken together, the time-dependent XPS data show that ODPa adsorption on PDMS-grafted as-built AlSi10Mg is already initiated within the first minutes of exposure and is accompanied by a pronounced reduction of silicon-containing surface species. The decrease in Si2p and the ratio Si2p/Al2p, together with the increase in P2s and C1s, points toward a competitive adsorption or exchange process rather than simple ODPa overlayer formation.

To further evaluate whether the compositional changes observed by XPS are accompanied by molecular changes within the organic interphase, PM-IRRAS measurements were performed during ODPa adsorption on PDMS-pretreated AlSi10Mg surfaces. Since PM-IRRAS requires a sufficiently reflective surface for reliable detection of ultrathin organic films, these measurements were carried out on polished AlSi10Mg substrates rather than on the rough as-built surfaces. Although this surface state differs from the as-built AM surface, the experiment provides qualitative insight into the evolution of ODPa- and PDMS-related vibrational features during the adsorption process.

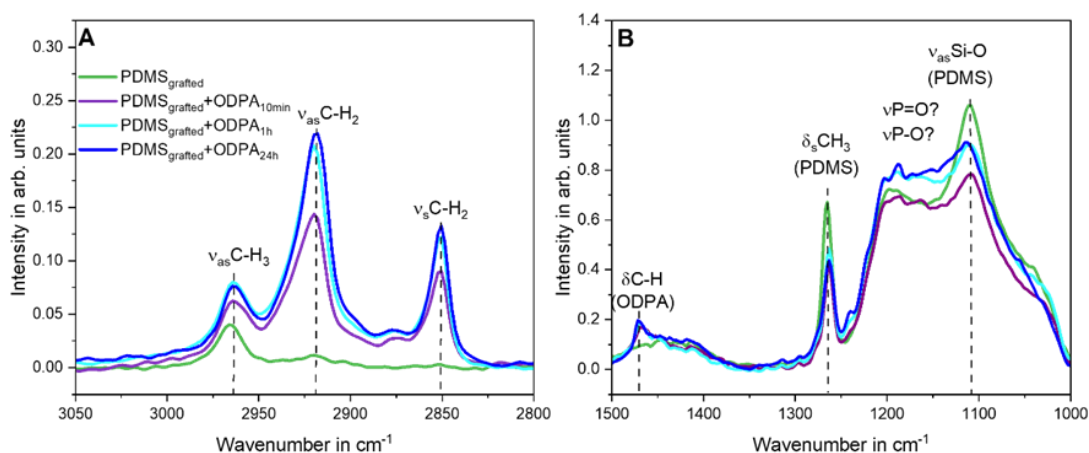


Figure 33. PM-IRRAS results of ODPa adsorption as function of time on PDMS-grafted (polished) AlSi10Mg surfaces. Image A shows the C-H stretching region in the wavenumber range between 3050 cm^{-1} and 2800 cm^{-1} . Image B shows the fingerprint region between 1500 cm^{-1} and 1000 cm^{-1} . Reproduced from: Prübner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", *Materials Chemistry and Physics*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ No changes were made.

In the C-H stretching region shown in Figure 33A, successful PDMS grafting is indicated by an absorption band at 2966 cm^{-1} , which is assigned to the asymmetric stretching vibration of methyl groups, $v_{as}(\text{CH}_3)$, in PDMS.^{178,179} After ODPa adsorption, this band remains visible but is slightly shifted to 2964 cm^{-1} and increases in intensity. This increase is most likely caused by overlapping C-H stretching contributions from both the PDMS methyl groups and the ODPa terminal CH_3 group. In addition, two new strong absorption bands appear after ODPa exposure at 2919 cm^{-1} and 2850 cm^{-1} , which are assigned to the asymmetric and symmetric CH_2 stretching vibrations,

$\nu_{as}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$, of the ODPA alkyl chain, respectively.^{85,177 180} The position of these bands indicates a highly ordered, crystalline-like arrangement of the ODPA alkyl chains.^{181,182} The increase in the C–H stretching intensities during ODPA adsorption can, in principle, originate from two contributions: an increasing amount of ODPA-derived alkyl chains at the surface and/or a change in the orientation of the corresponding transition dipole moments with respect to the surface normal. According to the IRRAS surface selection rule (see Section 2.4.1.1) and the applied polarization-modulation, the detected intensity is not solely proportional to the number of adsorbed molecules, but also depends on molecular orientation (see eq. (2-20)). Therefore, the intensity increase observed between 10 min and longer ODPA adsorption times cannot be interpreted exclusively as a coverage effect without further consideration.

In principle, the orientation of the ODPA alkyl chains may be estimated from the intensity ratio of the CH_2 and CH_3 stretching vibrations using the relation described in eq. (2-20). However, in the present system, a reliable quantitative determination is complicated by the overlap of the ODPA-related CH_3 signal with the CH_3 contribution of residual PDMS. To obtain an approximate ODPA-specific CH_3 intensity, the CH_3 contribution of the PDMS-grafted reference spectrum was subtracted from the ODPA-containing spectra. This approach yielded apparent alkyl-chain tilt angles between approximately 42 ° and 48 °. For comparison, Maxisch et al. found a tilt angle of about 17 – 18° on smooth alumina surfaces.⁸⁵ Bram et al. found an α value of approximately 31 ° for the same molecule on an AlMg1 alloy after 66 h of adsorption.⁸²

However, our calculated values should be interpreted with caution, because the XPS results indicate that the PDMS contribution changes during ODPA adsorption. Thus, a simple linear subtraction of the initial PDMS spectrum may introduce additional uncertainty.

Nevertheless, the estimated tilt angles show only minor variation as a function of ODPA adsorption time. This suggests that the pronounced increase in C–H stretching intensity after longer adsorption times is unlikely to be dominated by a systematic change in alkyl-chain orientation. Instead, the spectral evolution is primarily attributed to an increasing amount of ODPA-derived alkyl chains at the surface. The comparatively high apparent tilt angles further indicate that the ODPA alkyl chains are not oriented close to the surface normal, but adopt a more inclined arrangement, which may reflect the mixed PDMS/ODPA character of the interphase and the heterogeneous nature of the underlying AlSi10Mg surface.

The fingerprint region shown in Figure 33B provides further evidence for changes within the PDMS-derived interphase during ODPA adsorption. The absorption band at 1263 cm^{-1} , assigned to symmetric Si– CH_3 bending vibrations ($\delta_s(\text{CH}_3)$), of PDMS,^{44,178,179} decreases strongly after 10 min of ODPA adsorption and remains at a low intensity for longer adsorption times. This observation is consistent with the XPS results, which indicate a rapid decrease of PDMS-related silicon contributions during the initial stage of ODPA exposure. A more detailed interpretation of this spectral change should be made with caution, since the PM-IRRAS measurements were performed on polished AlSi10Mg reference surfaces, which differ substantially from the rough as-built AM surface investigated by XPS.

Two additional prominent bands are observed in the fingerprint region. The band at 1468 cm^{-1} is assigned to C–H bending vibrations, $\delta(\text{CH}_3)$, associated with ODPA,¹⁸⁰ whereas the band at 1109 cm^{-1} is attributed primarily to asymmetric Si–O stretching vibrations, $\nu_{as}(\text{Si–O})$, of PDMS.^{178,179} The ODPA-related $\delta(\text{CH}_3)$ band shows no pronounced dependence on adsorption time, since its maximum intensity is already reached after 10 min of ODPA exposure. In contrast, the $\nu_{as}(\text{Si–O})$ band decreases markedly after the first ODPA adsorption interval but increases again

at longer adsorption times, accompanied by the formation of a shoulder at higher wavenumbers. This behavior may be caused by overlapping contributions of PDMS-related Si–O vibrations and the growing amount of phosphonate-related P=O or P–O stretching vibrations in the spectral region between 1100 cm^{-1} and 1200 cm^{-1} .^{177,183} However, since the peak intensities measured by PM-IRRAS can be influenced by both the number and the relative orientation of the molecules bound to the surface, it is not possible to draw a definitive conclusion on this matter without further analysis.

The peak development at 1267 cm^{-1} can not be interpreted without caution, because ODPa could also participate in adsorption intensity here. However, in literature this peak is not consistently reported for ODPa adsorbed on aluminum oxides measured by PM-IRRAS.¹⁸³ Therefore, the peak at 1267 cm^{-1} is not used as a primary indicator for ODPa adsorption in the present discussion.

Overall, the PM-IRRAS results support the interpretation derived from the time-dependent XPS data. ODPa-related alkyl-chain vibrations appear already after short adsorption times, while PDMS-associated vibrational features change simultaneously. Thus, the spectra indicate a rapid ODPa-induced modification of the PDMS-derived interphase. In combination with the XPS results, this supports the assumption that ODPa adsorption is accompanied by partial reorganization of the pre-existing PDMS layer.

4.1.5. Model-substrate analysis of substrate-dependent PDMS/ODPa interfacial reorganization

The time-dependent XPS and PM-IRRAS results indicate that ODPa adsorption on PDMS-pretreated AlSi10Mg is accompanied by a partial reorganization of the PDMS-derived interphase. However, these measurements on the heterogeneous AM alloy do not allow an unambiguous assignment of this process to specific surface chemistries. To clarify whether the observed reorganization is related to Al-oxide- or SiO_x-rich surface sites, the sequential PDMS+ODPa modification was transferred to two simplified model substrates: a n-doped and polished Si wafer and a polished Al1050 alloy. Both substrate were treated with O₂-Plasma before XPS measurements.

The XP survey spectra quantification (survey spectra are shown in Figure S4 and Figure S5) summarized in Table 7 reveals a pronounced substrate dependence of the ODPa adsorption behavior. On the O₂-plasma-treated Si wafer, PDMS grafting increases the C1s contribution from 7.5 at% to 32.1 at%, while the Si2p signal decreases from 54.2 at% to 40.9 at%, confirming the formation of a PDMS-derived surface layer. Subsequent exposure to ODPa for 24 h does not lead to a detectable P2s signal. In addition, the C1s and Si2p contributions remain essentially unchanged, with values of 32.5 at% and 40.3 at%, respectively. This indicates that ODPa does not significantly adsorb onto the PDMS-grafted SiO_x-terminated surface under the applied conditions and that the PDMS layer remains stable on this substrate.

A different behavior is observed for the Al1050 model substrate. After O₂-plasma treatment, the surface is dominated by O1s and Al2p contributions, consistent with an oxidized aluminum surface. PDMS grafting leads to the appearance of a distinct Si2p contribution of 10.8 at%, confirming the presence of PDMS-derived species on the Al-oxide-covered surface. After subsequent ODPa exposure, a P2s signal of 1.0 at% is detected, while the C1s contribution increases markedly from 16.8 at% to 37.8 at%. At the same time, the Si2p signal decreases from

10.8 at% to 7.7 at%. These changes show that ODPA adsorption occurs on the PDMS-pretreated Al1050 surface and is accompanied by a reduction of the PDMS-related silicon contribution.

The comparison between both model substrates demonstrates that ODPA does not simply adsorb onto intact PDMS as a molecular overlayer. If ODPA adsorption on PDMS itself were the dominant mechanism, a P2s signal would also be expected after ODPA exposure of the PDMS-grafted Si wafer. Since this is not observed, the data indicate that ODPA adsorption requires access to suitable substrate-related binding sites and is promoted by Al-oxide-rich surface chemistry.

However, the model-substrate results do not necessarily prove a direct displacement of covalently grafted PDMS by ODPA. Instead, they indicate that the accessibility and/or stability of the PDMS-derived interphase depends strongly on the underlying oxide chemistry. On SiO_x-rich surfaces, PDMS appears to form a stable interphase that prevents detectable ODPA adsorption. On Al-oxide-rich surfaces, the PDMS coverage may be less dense or less stable, leaving reactive Al–OH/AlO_x sites accessible for ODPA adsorption. The observed decrease in the PDMS-related silicon contribution after ODPA exposure may therefore reflect partial removal or reorganization of weakly bound PDMS species, adsorption of ODPA at initially unoccupied AlO_x sites, or a combination of both processes.

Table 7. XPS-derived elemental quantification of PDMS and PDMS+ODPA modifications on Si wafer and Al1050 model substrates. The model substrates were used to evaluate the substrate dependence of ODPA adsorption on PDMS-pretreated SiO_x- and Al-oxide-rich surfaces. Values are given as atomic percentages obtained from survey spectra shown in Figure S4 and Figure S5. Adapted from Ref.¹¹⁵. The values are given in at%.

Surface condition	Core level									
	O1s	C1s	Si2p	P2s	Al2p	F1s	N1s	Ca2p	S2p	
Si-Wafer+30s O ₂ -Plasma	38.3	7.5	54.2	-	-	-	-	-	-	
Si-Wafer+30s O ₂ -Plasma+PDMS _{grafted}	27.0	32.1	40.9	-	-	-	-	-	-	
Si-Wafer+30s O ₂ -Plasma+PDMS _{grafted} +ODPA _{24h}	27.1	32.5	40.4	-	-	-	-	-	-	
Al1050+30s O ₂ -Plasma	50.0	16.8	-	-	29.3	1.8	0.4	0.2	1.5	
Al1050+30s O ₂ -Plasma+PDMS _{grafted}	42.2	21.4	10.8	-	24.4	0.9	0.3	0.1	-	
Al1050+30s O ₂ -Plasma+PDMS _{grafted} +ODPA _{24h}	33.1	37.8	7.7	1.0	19.8	0.6	0.1	-	-	

4.1.6. Wetting stability and electrochemical barrier properties during chloride exposure

After the chemical composition and interfacial reorganization of the PDMS- and ODP- modified surfaces had been characterized by XPS, PM-IRRAS, and water contact angle measurements, the corrosion-related stability of the resulting nanofilms was evaluated under chloride-containing aqueous exposure. This step is essential because the successful formation of a hydrophobic organic interphase does not necessarily imply that the film remains stable or electrochemically protective in contact with an aggressive electrolyte.

In a first step, the modified as-built AM AlSi10Mg surfaces were exposed to 0.05 M NaCl solution for defined immersion intervals and subsequently analyzed ex situ by water contact angle measurements. These measurements were used to assess whether chloride-containing aqueous exposure affects the low-surface-energy character of the films, for example through corrosion-induced surface changes, partial film detachment, hydrolytic degradation, or electrolyte-induced reorganization of the organic interphase.

In a second step, electrochemical impedance spectroscopy was used to evaluate the electrochemical barrier properties of the same surface states. While water contact angle measurements provide information on the outer wetting behavior, they do not directly reveal whether water or ions can penetrate through defects or nanoscale pathways within the film. EIS therefore complements the wettability analysis by probing the time-dependent electrochemical response of the modified alloy/electrolyte interface.

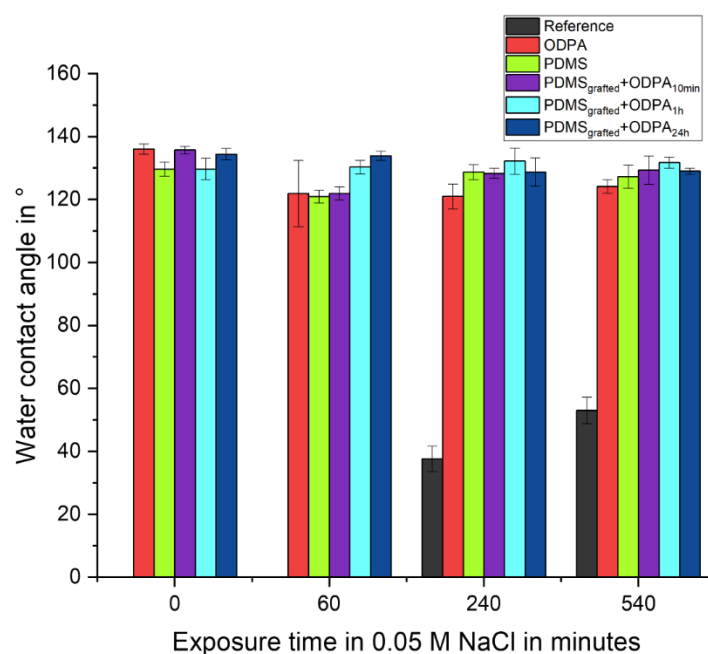


Figure 34. Ex-situ water contact angle measurements of as-built AM AlSi10Mg surfaces after chloride exposure. Water contact angles of the reference and modified surface states were measured before exposure (see Table 6) and after cumulative immersion intervals of 1 h, 4 h, and 9 h in 0.05 M NaCl solution. Error bars represent the standard deviation from at least three measurements. For the O_2 -plasma-activated reference surface, contact angles could not be determined before exposure and after 1 h due to immediate spreading of the water droplet. Reproduced from: Prüßner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", Materials Chemistry and Physics, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ The coloring of the figure and the caption has been changed.

The ex-situ water contact angle measurements after chloride exposure are shown in Figure 34. The O_2 -plasma-activated Reference surface exhibits a strongly hydrophilic behavior (as already depicted in Table 6), and contact angle values could not be determined for the initial state and after 1 h of immersion due to immediate spreading of the water droplet. After longer exposure times, measurable contact angles are obtained for the Reference surface, which can be attributed to corrosion-induced changes, partial surface passivation, or adsorption of adventitious species during the exposure and drying procedure. Nevertheless, the Reference surface remains clearly more hydrophilic than the organically modified surfaces.

In contrast, all ODPA-, PDMS-, and PDMS+ODPA-modified surfaces show high water contact angles throughout the entire exposure sequence. The contact angles remain in the range of approximately 120–135 ° after immersion in 0.05 M NaCl solution, demonstrating that the low-surface-energy character of the modified surfaces is largely preserved during chloride-containing aqueous exposure independent of the subsequent ODPA adsorption time on pre-grafted PDMS surfaces. This indicates that neither immediate film detachment nor complete hydrolytic degradation of the organic interphase occurs within the investigated exposure time.

Surely, this property provide an important prerequisite for corrosion protection (especially for atmospheric corrosion protection, see Section 2.1.4.3), but the actual ability of the films to suppress also electrolyte access and interfacial charge-transfer processes is assessed in the following by electrochemical impedance spectroscopy.

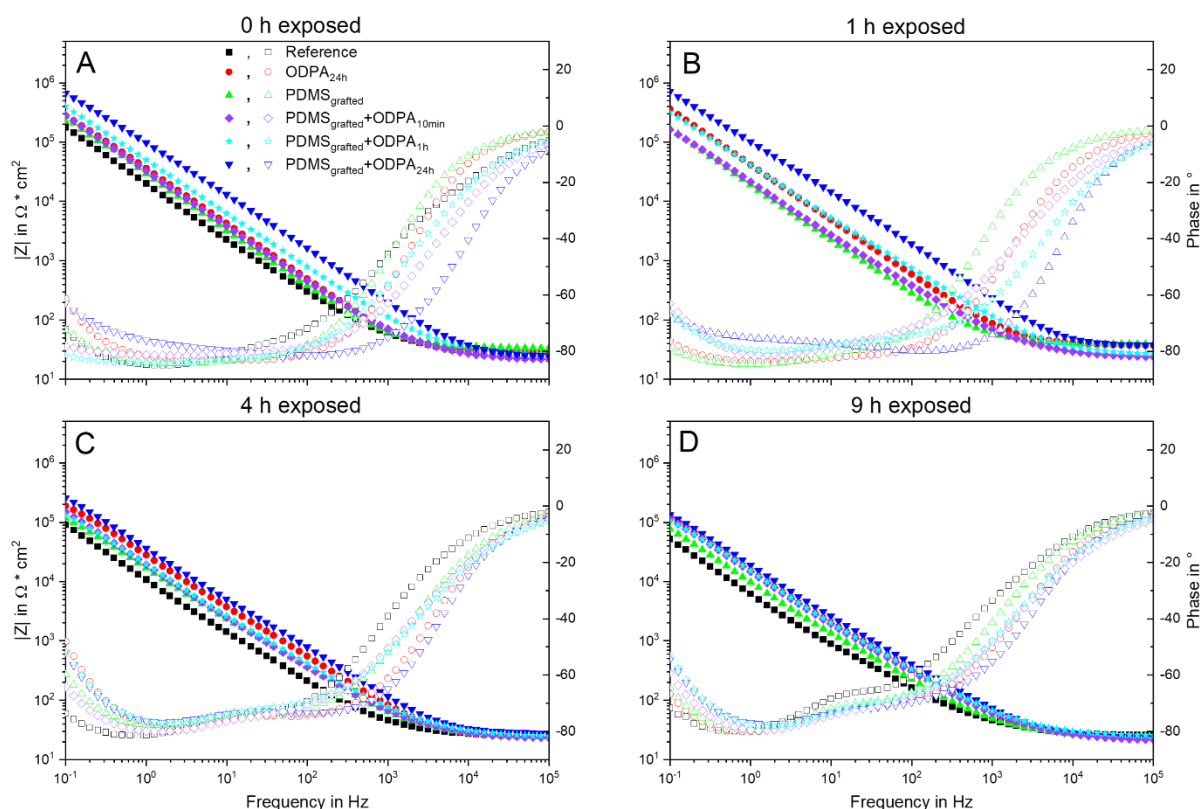


Figure 35. Electrochemical impedance spectra of Reference and modified as-built AM AlSi10Mg surfaces during chloride exposure. EIS spectra were recorded using the droplet-cell setup shown in Figure 24 for the initial surface states and after cumulative immersion intervals of 1 h, 4 h, and 9 h in 0.05 M NaCl solution. Image A shows the initial state before chloride exposure, image B after 1 h, image C after 4 h, and image D after 9 h cumulative immersion. Filled symbols represent the impedance modulus, while open symbols show the corresponding phase angle. The investigated surface states include the Reference surface, ODP A, PDMS, and sequential PDMS+ODPA modifications with ODP A adsorption times of 10 min, 1 h, and 24 h. Reproduced from: Prübner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", *Materials Chemistry and Physics*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ The wording of the caption has been adjusted.

The EIS spectra in Figure 35 show that the organic surface modifications influence the electrochemical response of the as-built AM AlSi10Mg surface. For a quantitative comparison, the impedance modulus at 0.1 Hz was extracted from the spectra and is summarized in Table 8. In the initial state, the unmodified reference surface (no previous O₂-Plasma treatment) exhibits an impedance of $1.48 \cdot 10^5 \Omega \cdot \text{cm}^2$. All modified surfaces show higher low-frequency impedance values, indicating reduced electrochemical accessibility of the alloy surface after ODP A adsorption, PDMS grafting, or sequential PDMS+ODPA treatment. The highest initial impedance is observed for the PDMS+ODPA_{24h} surface, with $8.90 \cdot 10^5 \Omega \cdot \text{cm}^2$, corresponding to an approximately sixfold increase compared with the Reference. This demonstrates that the combined organic interphase provides the most effective initial barrier among the investigated surface states.

Table 8. Low-frequency impedance values of Reference and modified as-built AM AlSi10Mg surfaces during chloride exposure. The impedance modulus at 0.1 Hz was extracted from the EIS spectra recorded before exposure and after cumulative immersion intervals of 1 h, 4 h, and 9 h in 0.05 M NaCl solution. Values are given as mean $\pm$ standard error of the mean from measurements at different surface positions on the same sample. Adapted from Ref. ¹¹⁵.

Surface condition	Z at 0.1 Hz in ($\Omega \cdot \text{cm}^2$) $\cdot 10^5$			
	0 h	1 h	4 h	9 h
Reference	1.48 $\pm$ 0.28*	-	0.81 $\pm$ 0.1	0.58 $\pm$ 0.06
ODPA	2.71 $\pm$ 0.04	3.97 $\pm$ 0.24	1.74 $\pm$ 0.10	1.24 $\pm$ 0.01
PDMS	2.26 $\pm$ 0.32	1.7 $\pm$ 0.01	1.4 $\pm$ 0.14	0.77 $\pm$ 0.11
PDMS+ODPA _{10min}	2.33 $\pm$ 0.51	1.39 $\pm$ 0.24	1.4 $\pm$ 0.1	1.12 $\pm$ 0.02
PDMS+ODPA _{1h}	3.40 $\pm$ 0.56	2.47 $\pm$ 0.45	1.23 $\pm$ 0.08	1.03 $\pm$ 0.06
PDMS+ODPA _{24h}	8.9 $\pm$ 0.7	6.18 $\pm$ 0.67	2.39 $\pm$ 0.20	1.56 $\pm$ 0.15

*This value is obtained on as-built AlSi10Mg surface without previous treatment with O₂-plasma for better comparison.

The individual ODPA- and PDMS-modified surfaces also improve the initial impedance, although less strongly. ODPA adsorption results in $2.71 \cdot 10^5 \Omega \cdot \text{cm}^2$, while PDMS grafting leads to $2.26 \cdot 10^5 \Omega \cdot \text{cm}^2$. The sequential modifications with shorter ODPA adsorption times show intermediate values, with $2.33 \cdot 10^5 \Omega \cdot \text{cm}^2$ for PDMS+ODPA_{10min} and $3.40 \cdot 10^5 \Omega \cdot \text{cm}^2$ for PDMS+ODPA_{1h}. Thus, the initial barrier performance increases most clearly when the PDMS-grafted surface is exposed to ODPA for 24 h, which is consistent with the previously discussed XPS and PM-IRRAS results indicating the formation of an ODPA-containing, reorganized organic interphase.

After 1 h of immersion in 0.05 M NaCl solution, the PDMS_{grafted}+ODPA_{24h} surface still exhibits the highest impedance, with $6.18 \pm 0.67 \cdot 10^5 \Omega \cdot \text{cm}^2$. The ODPA-modified surface shows $3.97 \pm 0.24 \cdot 10^5 \Omega \cdot \text{cm}^2$, while the PDMS-modified surface decreases to $1.70 \pm 0.01 \cdot 10^5 \Omega \cdot \text{cm}^2$. The shorter sequential modifications show lower values of $1.39 \pm 0.24 \cdot 10^5 \Omega \cdot \text{cm}^2$ for PDMS+ODPA_{10min} and $2.47 \pm 0.45 \cdot 10^5 \Omega \cdot \text{cm}^2$ for PDMS+ODPA_{1h}. These values indicate that the barrier effect remains most pronounced for the combined modification with the longest ODPA adsorption time during the early exposure stage.

With increasing immersion time, the impedance values of all surface states decrease, indicating progressive electrolyte access to the film-covered oxide interface and a gradual loss of barrier performance. After 4 h, the reference surface exhibits only $0.81 \pm 0.10 \cdot 10^5 \Omega \cdot \text{cm}^2$, whereas the modified surfaces remain higher. The PDMS+ODPA_{24h} surface still shows the highest value of

$2.39 \pm 0.20 \cdot 10^5 \Omega \cdot \text{cm}^2$, followed by ODPA with $1.74 \pm 0.10 \cdot 10^5 \Omega \cdot \text{cm}^2$. PDMS and PDMS+ODPA_{10min} both reach approximately $1.40 \cdot 10^5 \Omega \cdot \text{cm}^2$, while PDMS+ODPA_{1h} shows $1.23 \pm 0.08 \cdot 10^5 \Omega \cdot \text{cm}^2$. After 9 h, the overall impedance level is further reduced. Nevertheless, all modified surfaces remain above the reference value of $0.58 \pm 0.06 \cdot 10^5 \Omega \cdot \text{cm}^2$. The highest impedance is again obtained for PDMS+ODPA_{24h} with $1.56 \pm 0.15 \cdot 10^5 \Omega \cdot \text{cm}^2$, followed by ODPA, PDMS+ODPA_{10min}, PDMS+ODPA_{1h} and PDMS.

Overall, the EIS results indicate that the PDMS- and ODPA-based modifications improve the initial barrier properties of as-built AM AlSi10Mg. The sequential PDMS_{grafted}+ODPA_{24h} treatment provides the strongest protection at all investigated exposure times, but the continuous decrease in impedance shows that the protective effect is transient. The nanofilms therefore act primarily by reducing the initial electrolyte accessibility of the heterogeneous AM surface rather than by forming a permanently blocking coating under continuous chloride immersion.

Equivalent circuit fitting was applied to obtain a more detailed interpretation of the impedance response. The fitting strategy followed the principle of using the simplest circuit that adequately represents the electrochemical system. The corresponding spectra, fitted curves, and circuit diagrams are provided in Figure S6 in the Supporting Information, while the extracted fitting parameters are summarized in Table 9. In the initial state, the phase angle plots of the modified surfaces show a broad capacitive response without clearly separated time constants. Therefore, the spectra were described by a simplified Randles-type circuit consisting of the electrolyte resistance R_{ely} in series with a parallel $R_{\text{film}} || CPE_{\text{film}}$ element. This circuit represents the resistive and non-ideal capacitive behavior of the native oxide or organic-film-covered oxide layer. The use of a constant phase element instead of an ideal capacitance accounts for the pronounced roughness and chemical heterogeneity of the as-built AM AlSi10Mg surface. For the unmodified Reference surface, the simplified one-time-constant circuit was not sufficient even at short immersion times, indicating earlier electrolyte access and a less effective barrier response compared with the modified surfaces.

After prolonged chloride exposure, the phase angle plots evolve toward two distinguishable capacitive contributions. To describe this behavior, the circuit was extended by an additional $R_{\text{ct}} || CPE_{\text{dl}}$ element, representing charge-transfer processes and double-layer formation at electrochemically accessible sites. This transition indicates that the electrolyte partially penetrates or modifies the initially protective film/oxide interphase, so that the impedance response is no longer governed solely by the barrier layer but increasingly by interfacial electrochemical reactions.

Table 9. Equivalent circuit fitting parameters of reference and modified as-built AM AlSi10Mg surfaces before and after chloride exposure. Fits were performed for EIS spectra recorded in the initial state and after 9 h cumulative immersion in 0.05 M NaCl solution. The fitted parameters describe the resistance and capacitive behavior of the film-covered oxide/electrolyte interface and, after prolonged exposure, the charge-transfer-related response. The corresponding EIS spectra and fit curves are shown in Figure S6 in the Supporting Information. Reproduced from: Prüßner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", Materials Chemistry and Physics, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ The wording of the caption has been adjusted.

Surface condition	time (h)	R_{film} ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_{\text{film}} \cdot 10^{-6}$ ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n_{film}	R_{ct} ($\text{k}\Omega \cdot \text{cm}^2$)	$\text{CPE}_{\text{dl}} \cdot 10^{-6}$ ($\text{S} \cdot \text{cm}^{-2} \cdot \text{s}^n$)	n_{dl}	R_{ely} ($\Omega \cdot \text{cm}^2$)	$\chi^2 \cdot 10^{-4}$
Reference	0	682.1	8.4	0.97	1.3	397.2	0.51	20.3	2.2
	9	0.8	163.0	0.64	196.0	28.8	0.97	24.9	3.1
ODPA	0	758.3	5.0	0.93	-	-	-	30.0	1.5
	9	0.9	62.1	0.72	381.6	11.7	0.95	23.6	0.2
PDMS	0	1243.9	6.2	0.94	-	-	-	35.1	20.0
	9	0.8	109.0	0.68	216.2	18.3	0.95	24.2	1.1
PDMS+ODPA _{24h}	0	1839.6	1.9	0.90	-	-	-	24.3	12.0
	9	0.8	59.0	0.71	270.9	9.6	0.93	23.0	0.3

From data shown in Table 9, the impedance response in the initial state (0 h exposure) is dominated by the film-covered oxide layer. The fitted R_{film} values are higher for the modified surfaces than for the Reference, confirming the barrier effect of the organic modifications. The highest R_{film} is obtained for the PDMS+ODPA-modified surface, consistent with its highest low-frequency impedance. After 9 h of chloride exposure, R_{film} decreases markedly for all surface states to values close to $0.8\text{--}0.9\text{ k}\Omega\cdot\text{cm}^2$, indicating that the initially protective film-covered oxide structure has been strongly affected by electrolyte penetration. At the same time, charge-transfer-related contributions become necessary to describe the spectra, which indicates that electrochemical reactions occur at accessible sites within or underneath the modified oxide layer.

The results obtained by EIS are particularly important in view of the WCA measurements. Although the modified surfaces retain a hydrophobic outer character after immersion, the equivalent circuit analysis shows that the electrochemical interface evolves substantially during chloride exposure. Thus, the organic modifications remain effective in reducing initial electrolyte access, but they do not prevent progressive permeation of water and ions through the nanofilm-covered heterogeneous surface.

4.1.7. Proposed model of PDMS/ODPA interfacial organization and electrolyte permeation

The combined results of the microscopic, spectroscopic, wettability, and electrochemical analyses allow a mechanistic model for the PDMS/ODPA modification of as-built AM AlSi10Mg to be proposed. The as-built surface does not provide a smooth and chemically uniform oxide substrate. Instead, it is characterized by multiscale roughness, attached or partially molten particles, local defects, and a heterogeneous distribution of Al-, Si-, and O-containing surface regions. Consequently, the formation of an organic nanofilm on this surface must be understood as a local interfacial process rather than as adsorption on an ideal homogeneous oxide layer.

XPS and PM-IRRAS confirm that both PDMS and ODPA can be introduced onto the as-built AM AlSi10Mg surface. However, the sequential PDMS+ODPA modification does not result in a simple bilayer structure in which ODPA is deposited on top of an unchanged PDMS film. The time-dependent XPS results show a decrease in the Si2p/Al2p ratio during ODPA adsorption, while PM-IRRAS reveals the rapid appearance of ODPA-related alkyl-chain vibrations together with changes in PDMS-related vibrational features. These observations indicate that ODPA adsorption is accompanied by a partial reorganization of the PDMS-derived interphase.

The model-substrate experiments provide the chemical basis for assigning this reorganization to the local oxide chemistry of the substrate. On SiO_x -rich surfaces, PDMS remains comparatively stable and subsequent ODPA adsorption is not detected by XPS. In contrast, on Al-oxide-rich surfaces, ODPA adsorption occurs on PDMS-pretreated substrates and is accompanied by an increase in C1s and P2s contributions as well as a decrease in PDMS-related silicon signals. This suggests that PDMS forms a more stable and/or denser interphase on SiO_x -rich regions, whereas Al-oxide-rich sites remain more accessible to ODPA or allow partial reorganization of weakly bound PDMS-derived species.

Based on these findings, the final PDMS+ODPA-modified AM AlSi10Mg surface is best described as a chemically differentiated organic nanointerphase. PDMS-derived species are expected to remain preferentially associated with Si- or SiO_x -rich surface regions, while ODPA-derived

molecules preferentially address accessible Al-oxide-rich domains. This local differentiation is a direct consequence of the chemical heterogeneity of the as-built AM surface and explains why the combined modification provides a stronger initial barrier response than the individual PDMS or ODPa treatments.

The corrosion-related measurements further refine this model. Water contact angle measurements show that the organic modifications retain a highly hydrophobic outer surface character during chloride exposure. However, EIS reveals a continuous decrease in impedance with increasing immersion time, and equivalent-circuit analysis shows a marked decrease in film resistance after prolonged exposure. These results indicate that the hydrophobic interphase remains present at the outer surface but does not fully prevent the penetration of water and hydrated ions through defects, pores, or nanoscale transport pathways.

The proposed model (see Figure 36) therefore consists of two coupled processes: first, a substrate-dependent formation and reorganization of a mixed PDMS/ODPA interphase on the heterogeneous AM AlSi10Mg surface; second, a time-dependent electrolyte permeation through this nanofilm-covered oxide structure during chloride exposure. The combined PDMS+ODPA treatment, especially after 24 h ODPa adsorption, provides the most effective initial barrier by reducing the accessibility of the alloy surface. Nevertheless, the protection is transient under continuous immersion and is better described as a short-term inhibition of electrolyte access rather than as a permanently blocking corrosion protection coating.

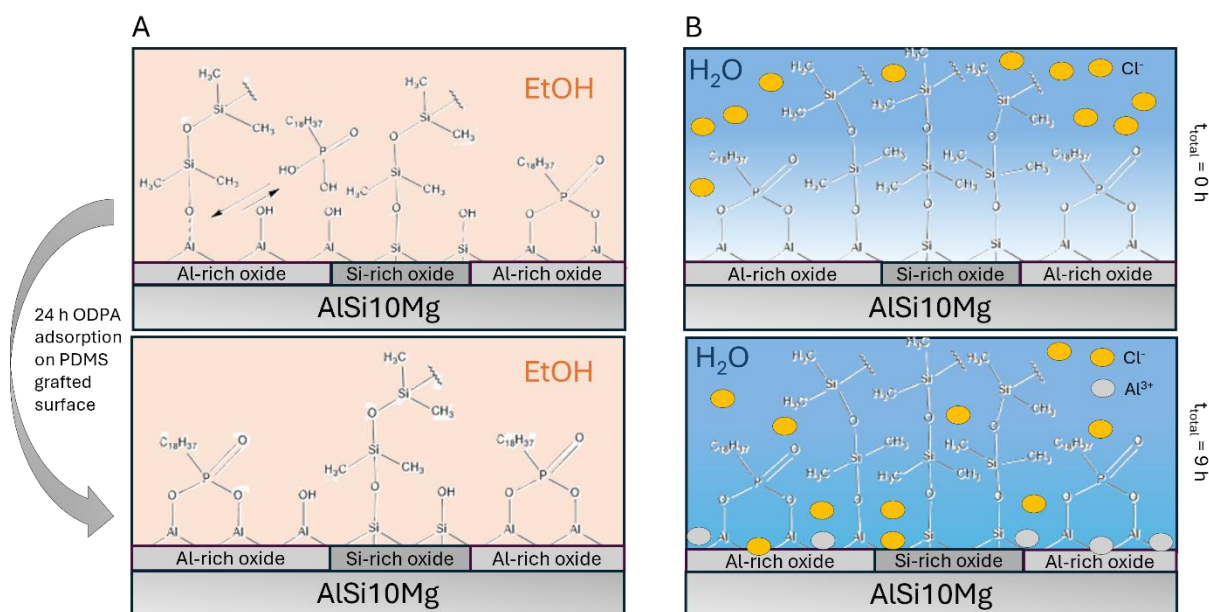


Figure 36. Proposed model of the PDMS/ODPA interphase formation and its evolution during chloride exposure on as-built AM AlSi10Mg. (A) Schematic illustration of the substrate-dependent reorganization of the organic interphase during ODPa adsorption from 1 mM ethanolic ODPa solution. PDMS-derived species remain preferentially associated with Si-rich oxide regions, whereas ODPa adsorption occurs preferentially at accessible Al-rich oxide sites, resulting in a chemically differentiated mixed PDMS/ODPA interphase. (B) Schematic illustration of the subsequent chloride exposure in 0.05 M NaCl solution. Water ingress (blue background) and chloride ions (yellow circles) progressively penetrate the mixed protective layer as a function of immersion time, while the hydrophobic outer surface character is largely retained. At longer immersion times, incipient corrosion processes may occur at accessible interfacial sites, as indicated by the release of Al³⁺-species (gray circles). Reproduced from: Pr  bner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", *Materials Chemistry and Physics*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ The wording of the caption has been adjusted.

4.1.8. Conclusion and implications for further surface design

The results of this section demonstrate that as-built AM AlSi10Mg surfaces can be successfully modified by ODPa adsorption, PDMS grafting, and sequential PDMS+ODPA treatment. Despite the pronounced topographical roughness and chemical heterogeneity of the as-built surface, all organic modifications strongly reduce surface wettability and improve the initial electrochemical barrier response. The combined PDMS+ODPA treatment, particularly after 24 h ODPa adsorption, provides the highest initial impedance and therefore the most effective short-term reduction of electrolyte accessibility.

At the same time, the results reveal important limitations of this approach. Based on the time-dependent XPS data, PM-IRRAS results, and model-substrate experiments, it appears likely that the sequential modification does not form a homogeneous bilayer, but rather a chemically differentiated interphase influenced by the local $\text{AlO}_x/\text{SiO}_x$ surface chemistry. However, the exact local arrangement of PDMS- and ODPa-derived species on the as-built AM surface could not be resolved unambiguously within the scope of this study. Moreover, the high water contact angles after chloride exposure show that the hydrophobic outer surface character is largely retained, whereas the decreasing impedance and fitted film resistance indicate progressive electrolyte permeation. Thus, the protective effect of the PDMS/ODPA modification is transient under continuous aqueous chloride exposure and should be understood as short-term inhibition rather than long-term immersion protection.

A further limitation arises from the intrinsic roughness and heterogeneity of the as-built surface itself. These surface characteristics not only complicate the adsorption and formation of homogeneous nanoscale films, but also affect the precision and interpretation of the applied characterization methods. In XPS, the analyzed signal represents an area-averaged composition over a topographically and chemically heterogeneous surface. In PM-IRRAS, the rough and weakly reflective as-built surface limits direct spectroscopic analysis and requires polished reference substrates for qualitative mechanistic insight. Similarly, electrochemical measurements on rough AM surfaces are affected by uncertainties in the true electrochemically active area, local electrolyte retention, and wetting states that may vary between Wenzel- and Cassie–Baxter-like regimes. Therefore, the derived surface compositions, contact angles, and impedance values should be interpreted as representative but system-specific descriptors rather than absolute material constants.

A further implication concerns the PDMS grafting strategy itself. In Section 4.1, PDMS was grafted using a UV-induced process, for which the exact surface-bonding mechanism remains difficult to resolve unambiguously. If the process were governed exclusively by non-selective radical reactions (see Section 2.3.2), a pronounced substrate dependence of the PDMS/ODPA interfacial behavior would not necessarily be expected. However, the model-substrate results suggest that the oxide chemistry of the underlying surface influences the stability and/or density of the PDMS-derived interphase. This observation motivates the use of a more controlled PDMS grafting approach in the following section, in which PDMS is grafted at room temperature without UV irradiation and combined with defined surface pretreatments and SiO_x -based interlayers.

These findings highlight the importance of controlling both surface chemistry and surface morphology for nanoscale corrosion protection of AM aluminum alloys. The as-built surface provides technological relevance but also imposes strong limitations on film homogeneity, mechanistic interpretation, and barrier integrity. Consequently, the following section investigates whether mechanical and chemical pretreatments, as well as the introduction of defined SiO_x -

based interlayers, can provide a more controlled substrate for PDMS-based surface functionalization. Based on the substrate-dependent PDMS stability observed in this section, SiO_x-CVD interlayers are considered as a promising adhesive layer concept to promote a more uniform and stable PDMS-derived interphase and improve the resulting corrosion-related performance.

4.2. PDMS grafting on AM AlSi10Mg with SiO_x-CVD adhesion layer

4.2.1. Motivation for controlled SiO_x/PDMS thin-film architectures

The results of Section 4.1 demonstrated that PDMS-derived species can be introduced onto as-built AM AlSi10Mg surfaces, but also revealed that the stability and composition of the resulting interphase depend on the local surface chemistry. In particular, the model-substrate experiments suggested that PDMS is more stable and/or more densely associated with SiO_x-rich surfaces than with Al-oxide-rich surfaces. At the same time, the UV-induced grafting approach used in Section 4.1 does not allow the exact bonding mechanism to be resolved unambiguously. If the process were governed exclusively by non-selective radical reactions, a pronounced dependence on the underlying oxide chemistry would not necessarily be expected. The observed substrate dependence therefore motivates a more controlled PDMS grafting strategy in which the role of surface chemistry can be assessed more directly.

For this reason, Section 4.2 investigates PDMS grafting at room temperature without UV irradiation on mechanically and chemically pretreated AM AlSi10Mg surfaces. Mechanical polishing was used to reduce the pronounced roughness of the as-built surface and to provide a more defined substrate for thin-film formation and analysis. Chemical etching was subsequently applied to expose the characteristic Al–Si microstructure more clearly and to increase the accessibility of Si-enriched surface regions. This approach was chosen to evaluate whether the intrinsic Si-containing microstructure of AlSi10Mg can promote PDMS attachment without the need for an additional adhesion layer.

In parallel, SiO_x-CVD interlayers were deposited on the same alloy surface as chemically defined adhesion-promoting layers for PDMS grafting. This concept is inspired by previous work in which SiO_x-CVD layers were used on non-SiO_x-terminated substrates to facilitate silicone grafting.⁴⁴ However, the chemical structure, electrochemical behavior, and corrosion-related stability of such SiO_x/PDMS architectures were not systematically assessed in that context. The present section therefore extends this approach by combining spectroscopic, wettability-based, and electrochemical characterization to clarify how a defined SiO_x interlayer affects PDMS attachment and the resulting barrier performance.

The central question addressed in this section is whether controlled surface pretreatment and SiO_x-CVD interlayer formation can improve the formation, stability, and corrosion-related performance of PDMS-based thin-film architectures on AM AlSi10Mg compared with direct PDMS grafting on the pretreated alloy surface.

4.2.2. Local surface heterogeneity of polished and etched AM AlSi10Mg

Mechanical polishing and subsequent chemical etching lead to a pronounced change in the surface morphology of AM AlSi10Mg compared with the as-built surface discussed in Section 4.1.2. As shown in Figure 37A, the low-magnification FE-SEM image reveals a significantly smoother and more defined surface, while laser scan tracks and associated heat-affected zones (HAZ; see Section 2.2.1 for details) can still be distinguished. Their orientation indicates that the

investigated surface is oriented perpendicular to the building direction, corresponding to the surface orientation used in Section 4.1.

A higher-magnification FE-SEM image recorded within one of these heat-affected regions is shown in Figure 37B. After etching, the characteristic dendritic microstructure of LPBF-manufactured AlSi10Mg becomes clearly visible. This network-like morphology is present across the investigated surface, although its local density and appearance vary depending on the local heat profile, melt pool overlap, and solidification conditions during the LPBF process. The observed structure can be assigned to an Al-rich matrix surrounded by Si-enriched eutectic regions (verified from EDS analysis shown in Figure 38), which is typical for rapidly solidified AlSi10Mg.

Figure 37C shows a high-magnification image of one of these dendritic/eutectic regions. The detailed view reveals fine, locally exposed microstructural features on the sub-micrometer scale. Thus, the applied polishing and etching procedure reduces the pronounced macroscopic roughness of the as-built surface, but at the same time exposes the intrinsic chemical and microstructural heterogeneity of the alloy. This surface state is therefore more suitable for studying the influence of local Al- and Si-rich regions on subsequent PDMS grafting and for comparing direct PDMS modification with the SiO_x-CVD interlayer approach.

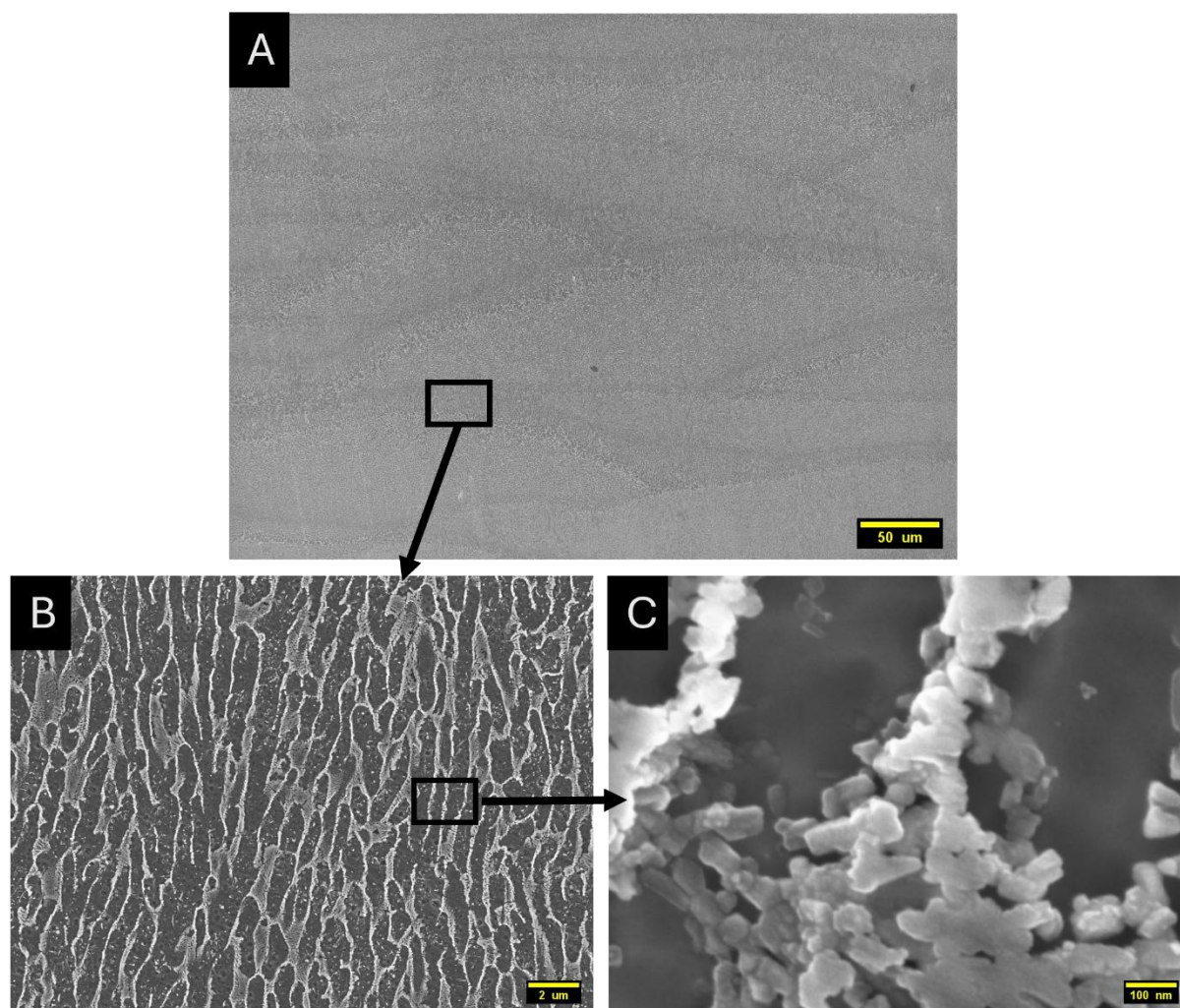


Figure 37. FE-SEM images of polished and etched AM AlSi10Mg surfaces at different magnifications. (A) In-lense-detector was used. Electron acceleration voltage was 2 kV. Low-magnification image showing laser scan tracks and associated heat-affected zones (HAZ). Their orientation indicates that the investigated surface is perpendicular to the building direction, as in Section 4.1. (B) In-lense-detector was used. Electron acceleration voltage was 4 kV. Higher-magnification image recorded in a representative HAZ region, revealing the characteristic dendritic Al-Si microstructure. (C) In-lense-detector was used. Electron acceleration voltage was 4 kV. High-magnification image recorded in a representative dendritic/eutectic region, showing fine eutectic features and locally exposed Si-enriched structures within the Al-rich matrix. The markings indicate representative regions used for higher-magnification imaging rather than identical surface positions.

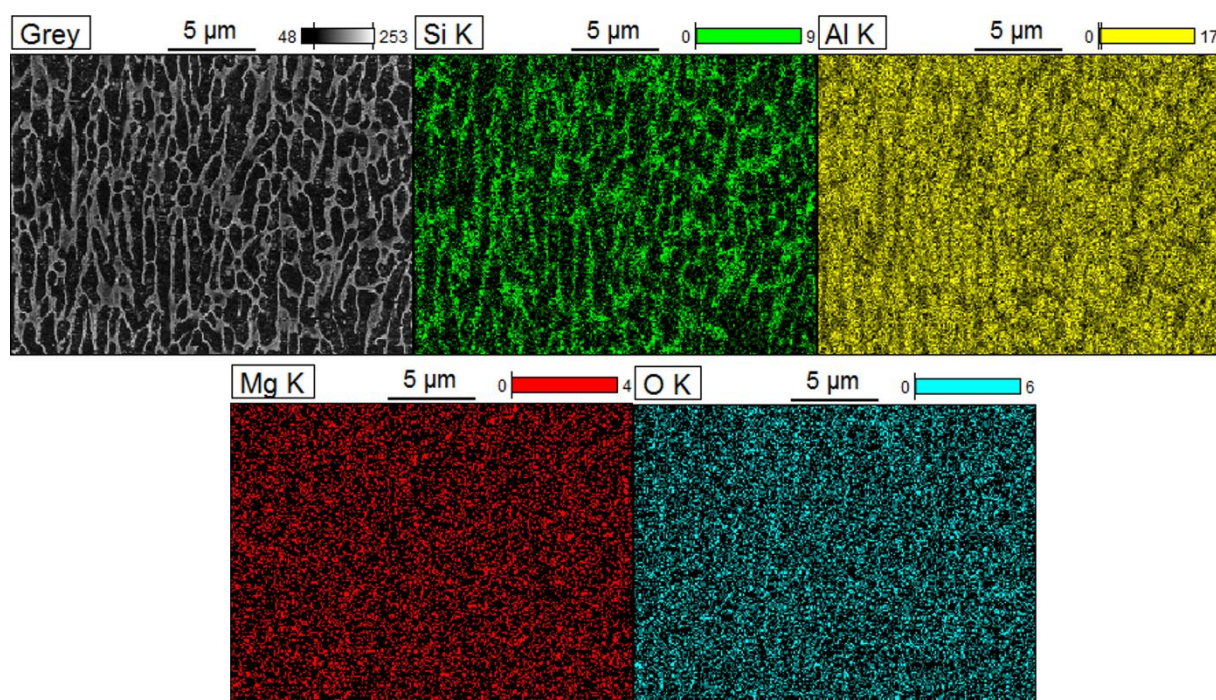


Figure 38. EDS analysis of the polished and etched AM AlSi10Mg surface. The grey-scale image shows the surface region used for EDS mapping. The elemental maps display the spatial distribution of the Si K, Al K, Mg K, and O K signals. The Si K map confirms the presence of Si-enriched network-like eutectic regions, whereas the Al K signal is broadly distributed over the matrix. The Mg K signal appears weak due to the low Mg content of the alloy. The O K signal indicates oxygen-containing regions within the analyzed near-surface volume and may include contributions from native surface oxides as well as process-related oxidized structures formed during LPBF manufacturing

The chemical heterogeneity revealed by FE-SEM is further supported by EDS mapping, as shown in Figure 38. The corresponding grey-scale image again displays the characteristic network-like microstructure of the polished and etched AM AlSi10Mg surface. The Si K map confirms that the network-like regions are enriched in silicon, whereas the Al K signal is distributed over the entire surface and is relatively more pronounced in the matrix regions between the Si-rich features. The Mg K signal appears weak and rather homogeneously distributed, which is consistent with the comparatively low Mg content of the alloy and does not allow a more detailed assignment of Mg-containing phases in this representation. The O K signal is broadly distributed across the investigated area.

Overall, the EDS results confirm that the polished and etched surface consists of an Al-rich matrix intersected by Si-enriched eutectic regions. Thus, the applied pretreatment exposes the intrinsic Al–Si microstructure of the LPBF-manufactured alloy while providing a smoother and more defined surface than the as-built state.

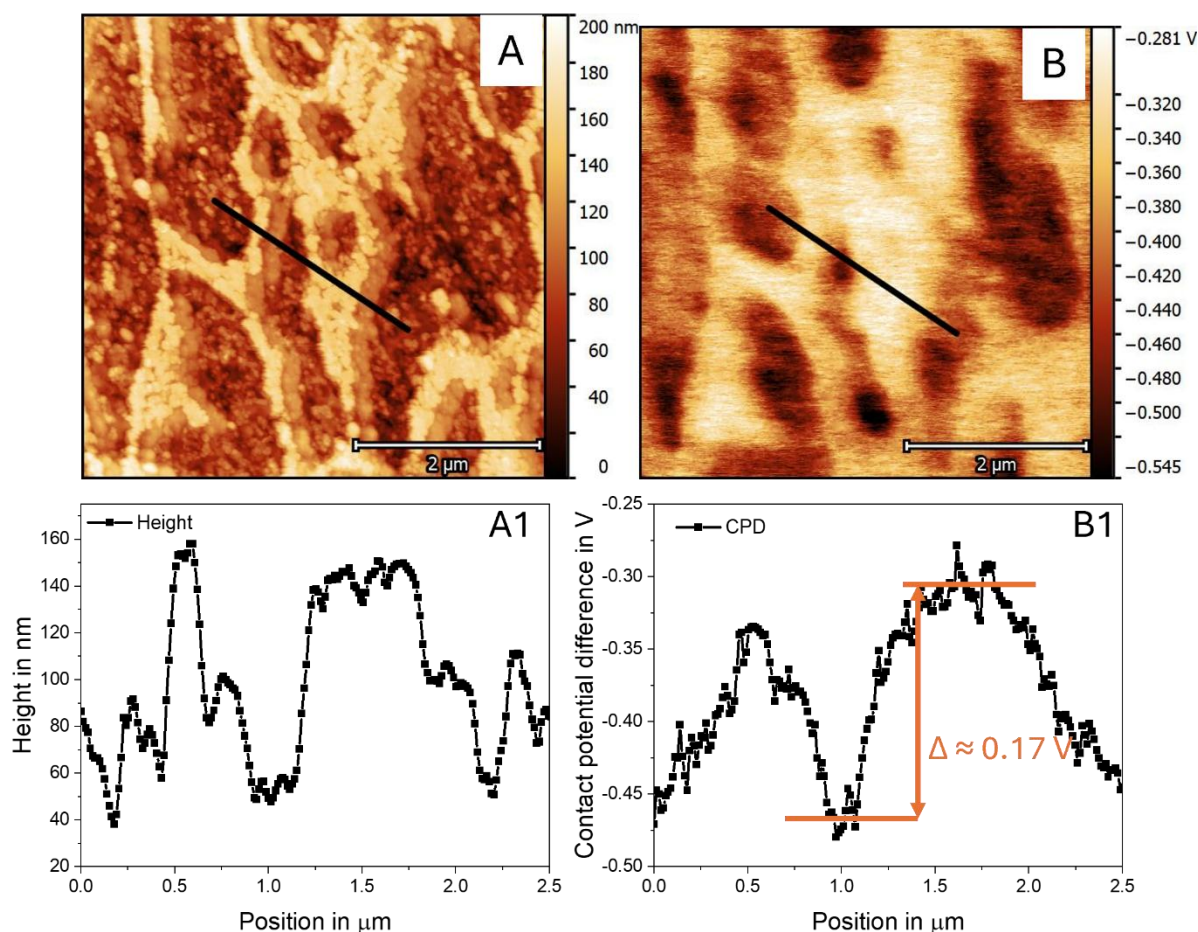


Figure 39. AFM and SKPFM analysis of polished and etched AM AlSi10Mg surfaces. (A) AFM height map of the polished and etched surface, showing the local topographical contrast associated with the exposed Al-Si microstructure. The indicated line profile is shown in (A1). (B) Corresponding SKPFM contact-potential-difference map recorded on the same surface region. The indicated line profile is shown as absolute contact-potential-difference values (CPD) in (B1). The SKPFM data reveal local CPD variations between the microstructural regions, with Si-enriched features pointing towards higher Volta potentials than the surrounding Al-rich matrix.

AFM and SKPFM measurements were used to further assess the local topographical and Volta-potential heterogeneity of the polished and etched AM AlSi10Mg surface. The AFM height map in Figure 39A shows a pronounced surface relief on the nanometer scale, which is consistent with the microstructural contrast observed by FE-SEM and EDS. The corresponding line profile in Figure 39A1 confirms local height variations between the exposed microstructural regions. These height differences are attributed to the different response of Al-rich and Si-enriched regions to the chemical etching procedure. The resulting topographical heterogeneity is reflected in an arithmetic mean surface roughness of $S_a = 31.2 \pm 1.7$ nm, calculated from two representative $5 \times 5 \mu\text{m}^2$ AFM height maps.

The corresponding SKPFM contact-potential map in Figure 39B reveals that the microstructural contrast is not only topographical, but also associated with local differences in surface electronic properties. The CPD profile in Figure 39B1 indicates that the Si-enriched regions exhibit a higher Volta potential than the surrounding Al-rich matrix. This observation is consistent with findings of Revilla et al.⁹⁶ It is likely that these potential heterogeneity may contribute to micro-galvanic driving forces under corrosive conditions.¹⁵⁸

In combination with the FE-SEM and EDS results, the AFM/SKPFM data show that polishing and etching provide a smoother and more experimentally accessible surface than the as-built state, while preserving a pronounced local heterogeneity in morphology, chemistry, and Volta potential.

This local heterogeneity is relevant for the subsequent thin-film modification strategy. The higher Volta potential of Si-enriched regions suggests that these areas may act as comparatively noble microstructural features, whereas adjacent Al-rich regions may be more susceptible to anodic dissolution when an electrolyte is present. At the same time, the exposure of Si-containing regions may be beneficial for PDMS attachment, as suggested by the substrate-dependent PDMS stability discussed in Section 4.1. Thus, the polished and etched surface provides a controlled but still chemically differentiated substrate for evaluating direct PDMS grafting and the additional effect of a SiO_x-CVD interlayer.

4.2.3. Spectroscopic and wettability-based characterization of SiO_x-CVD and PDMS-modified surfaces

In Section 4.2.2, the polished and etched AM AlSi10Mg surface was characterized with respect to its local morphology, chemical heterogeneity, and Volta-potential distribution. This surface state provides the substrate for the subsequent thin-film modifications and is therefore referred to as the Reference in the following. In this section, the formation of SiO_x-CVD interlayers, the direct grafting of PDMS, and the combined SiO_x-CVD+PDMS modification are investigated in order to evaluate how the surface chemistry and wettability of the pretreated AlSi10Mg surface are altered by each modification step.

A characterization strategy analogous to Section 4.1 is applied. First, PM-IRRAS is used to identify characteristic vibrational features of the SiO_x-CVD and PDMS-based surface modifications. Subsequently, XPS analysis is employed to quantify the elemental composition and to assess changes in the outermost surface region. Finally, water contact angle measurements are used to correlate the spectroscopic evidence of film formation with the resulting changes in surface wettability. This combined characterization provides the basis for comparing the chemical composition and wettability of directly PDMS-modified surfaces with those containing an additional SiO_x-CVD interlayer.

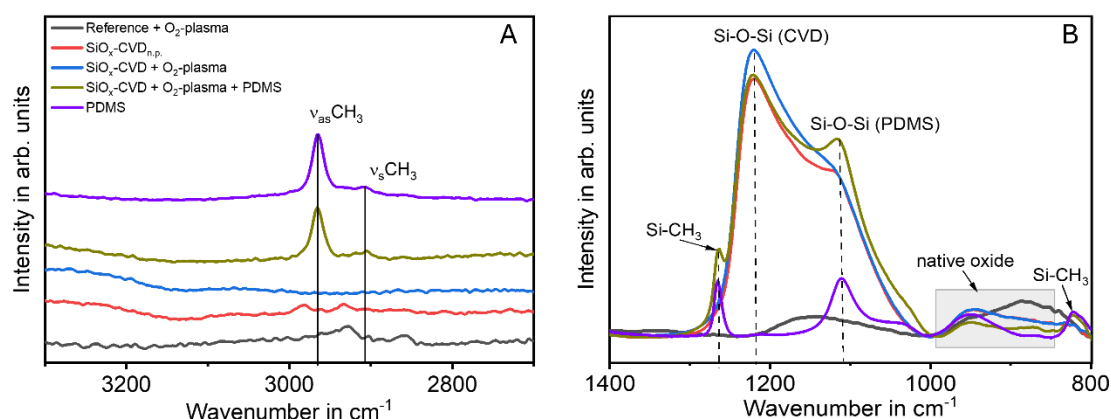


Figure 40. PM-IRRAS spectra of polished and etched AM AlSi10Mg surfaces after SiO_x -CVD deposition and PDMS grafting. (A) C-H_x stretching region between 3300 cm^{-1} and 2750 cm^{-1} . (B) Fingerprint region between 1400 cm^{-1} and 800 cm^{-1} . The investigated surface states include the Reference surface after O_2 -plasma treatment, SiO_x -CVD without subsequent O_2 -plasma treatment (" SiO_x -CVD_{n.p.}"), SiO_x -CVD after O_2 -plasma treatment, PDMS-grafted on Reference surface after O_2 -plasma treatment, and the combined SiO_x -CVD+PDMS modification. The intensity scales in (A) and (B) are not identical for clarity. Adapted from Ref.¹⁷⁰.

PM-IRRAS was first used to identify characteristic vibrational features of the SiO_x -CVD and PDMS-based surface modifications. The C-H_x stretching region is shown in Figure 40A. The polished and etched Reference surface exhibits only weak C-H_x absorption bands, which are attributed to residual hydrocarbon species remaining after the cleaning and plasma treatment. After SiO_x -CVD deposition without subsequent O_2 -plasma treatment (" SiO_x -CVD_{n.p.}"), C-H_x absorption bands are still visible, but their positions differ from those of the Reference surface. This indicates that organic residues from the CVD precursor, most likely incompletely reacted ethoxy groups, may still be present after the CVD process.

After applying an additional O_2 -plasma treatment to the SiO_x -CVD layer, the C-H_x absorption bands disappear. This again supports the assumption that the plasma treatment removes residual organic precursor fragments or organic contaminations. In contrast, both PDMS-containing surface states show pronounced C-H_x absorption bands. The dominant band at approximately 2965 cm^{-1} and the weaker contribution at approximately 2906 cm^{-1} are assigned to asymmetric and symmetric CH_3 stretching vibrations of PDMS, respectively, aligning with IR-spectra reported in Section 4.1.4.^{178,179} Their presence confirms the successful attachment of PDMS both directly on the Reference surface and on the SiO_x -CVD interlayer.

The fingerprint region in Figure 40B provides additional information on the inorganic SiO_x layer and the PDMS-derived interphase. The reference surface shows broad absorption features between approximately 1200 cm^{-1} and 1000 cm^{-1} , which can be assigned to oxyhydroxide-related surface species, while contributions below 1000 cm^{-1} are associated with oxide-related vibrations.^{114,184,185} The SiO_x -CVD_{n.p.} surface exhibits a pronounced Si-O-Si-related absorption band at approximately 1220 cm^{-1} with a shoulder around 1120 cm^{-1} , consistent with the formation of an oxidized Si-O-Si network.^{178,185} After O_2 -plasma treatment, the relative intensity of the band at 1220 cm^{-1} increases, which may indicate further oxidation or removal of residual organic precursor species from the SiO_x -CVD layer. However, according to the interpretation proposed by Dölle et al., this change should not be assigned to densification of the $\text{SiO}_x/\text{SiO}_2$ -CVD network, because densification would usually be accompanied by a shift of the Si-O-Si

stretching band toward higher wavenumbers.^{178,185} The observed spectral features therefore suggest that the SiO_x-CVD layer is highly oxidized but still porous.^{178,185}

For the PDMS-containing surfaces, additional characteristic absorption bands appear. The band at approximately 1264 cm⁻¹ is assigned to symmetric Si-CH₃ bending vibrations, the contribution around 1115 cm⁻¹ is attributed to asymmetric Si-O-Si stretching vibrations of the PDMS backbone and the band at approximately 823 cm⁻¹ is assigned to CH₃ rocking vibrations.^{178,179} These features are observed for both directly grafted PDMS and the combined SiO_x-CVD+PDMS modification, confirming that PDMS-derived species are present in both surface architectures. The IR absorption bands are summarized in Table 10.

Overall, the PM-IRRAS results demonstrate the successful formation of the individual SiO_x-CVD and PDMS modifications as well as the combined SiO_x-CVD+PDMS thin-film architecture. Thus, PM-IRRAS provides the first spectroscopic evidence that both direct PDMS grafting on the polished and etched AlSi10Mg surface and PDMS grafting on a SiO_x-CVD interlayer are feasible.

Table 10. Assignment of characteristic IR absorption bands observed in the PM-IRRAS spectra shown in Figure 40. The table summarizes the peak positions and corresponding vibrational modes used for the interpretation of the SiO_x-CVD and PDMS-based surface modifications applied on AM AlSi10Mg substrates. Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

Peak position in cm ⁻¹	Vibration mode ^[a]
2965	CH ₃ asymmetric stretching
2906	CH ₃ symmetric stretching
1264	(Si-)CH ₃ symmetric bending
1220	Si-O(-Si) asymmetric stretching (SiO _x -CVD)
1115 [shoulder]	Si-O(-Si) asymmetric stretching [SiO _x -CVD] (PDMS)
1032	Si-O(-Si) symmetric stretching (PDMS)
823	CH ₃ rocking (PDMS)

[a] Ref. ^{178,179,185,186}

After the vibrational characterization by PM-IRRAS, XP survey spectra analysis was used to quantify the elemental composition of the different surface states. The individual XP survey spectra are shown in Figure S7 in the Supporting Information. Quantification results are summarized in Table 11. For the polished and etched reference surface, the atomic composition is dominated by O1s and Al2p contributions of 47.1 ± 0.7 at% and 33.2 at%, respectively. In addition, a distinct Si2p contribution of 10.7 ± 0.1 at% is detected, reflecting the Si-containing microstructure of the AlSi10Mg alloy. The C1s content is comparatively low at 7.8 ± 0.5 at%, indicating that the applied O₂-plasma treatment strongly reduced carbonaceous surface contamination, which is in alignment with results obtained on as-built AlSi10Mg surfaces (see Section 4.1.3). Apart from EDS results shown in Figure 38, no Mg signal is detected within the XPS survey spectra, which is most likely related to the chemical pretreatment, since the acidic

desmutting step may promote preferential dissolution or depletion of Mg-containing surface species. Minor F1s and N1s contributions are also detected.

Table 11. XPS quantification (in at%) evaluated from survey spectra for unmodified (Reference) and modified (SiO_x-CVD, PDMS and SiO_x-CVD+PDMS) polished and etched AM AlSi10Mg surfaces. All values are reported as mean $\pm$ standard deviation based on the measurement of two to three different samples. The superscripts “†” or “‡” indicate the sequential treatment of a single sample in the following order: Reference, SiO_x-CVD and SiO_x-CVD+PDMS or Reference and PDMS, respectively. The values shown in brackets for the columns “PDMS”, “SiO_x-CVD” and “SiO_x-CVD+PDMS” represent the mean and standard deviation calculated from two to three measurements, which were not measured sequentially in all steps. Based on Ref.¹⁷⁰.

Core level	Reference (†,‡)	SiO _x -CVD (†)	PDMS (‡)	SiO _x -CVD+PDMS (†)
C 1s	7.8 $\pm$ 0.5	12.1 (15.6 $\pm$ 3.5)	20.3 (21.2 $\pm$ 2.1)	22.4 (26.5 $\pm$ 3.0)
O 1s	47.1 $\pm$ 0.7	49.7 (47.4 $\pm$ 2.3)	38.0 (37.7 $\pm$ 2.3)	39.1 (36.2 $\pm$ 2.1)
Si 2p	10.7 $\pm$ 0.1	15.5 (14.5 $\pm$ 1.1)	16.7 (16.8 $\pm$ 3.2)	20.5 (21.8 $\pm$ 1.1)
Al 2p	33.2 $\pm$ 0	21.1 (21.2 $\pm$ 0.1)	24.0 (23.5 $\pm$ 3.3)	17.5 (15.2 $\pm$ 1.9)
F 1s	1.0 $\pm$ 0	1.0 (0.8 $\pm$ 0.3)	0.7 (0.6 $\pm$ 0.4)	0.5 (0.3 $\pm$ 0.1)
N 1s	0.4 $\pm$ 0.1	0.5 (0.7 $\pm$ 0.2)	0.3 (0.2 $\pm$ 0.1)	- (0.1 $\pm$ 0.1)

After SiO_x-CVD deposition, the surface composition changes in agreement with the PM-IRRAS results. The Si2p contribution increases from 10.7 at% for the Reference surface to 15.5 at%, while the O1s contribution slightly increases from 47.1 at% to 49.7 at%. At the same time, the Al2p signal decreases markedly from 33.2 at% to 21.1 at%. This trend indicates the formation of a silicon oxide-containing overlayer, which partially attenuates the underlying Al- and most-likely also the Si-substrate signal. The C1s contribution also increases from 7.8 at% to 12.1 at%, which may originate from adventitious carbon or residual organic precursor fragments associated with incompletely reacted TEOS species. However, the absence of pronounced C–H_x bands in the PM-IRRAS spectrum after subsequent O₂-plasma treatment suggests that a large fraction of such organic residues is removed or oxidized during plasma activation. Therefore, the XPS quantification supports the formation of a thin, oxidized SiO_x-CVD layer on the Reference surface.

For the directly PDMS-modified surface, the XPS survey data show a pronounced increase in both C1s and Si2p contributions compared with the Reference surface. The C1s concentration increases from 7.8 at% to 20.3 at%, while the Si2p signal increases from 10.7 at% to 16.7 at%. The same trend is confirmed by the independently measured samples, which yield 21.1 at% for C1s and 16.8 at% for Si2p. In parallel, the O1s contribution decreases from 47.1 at% to 38.0 at% and the Al2p contribution decreases from 33.2 at% to 24.0 at%. This compositional change is consistent with the attachment of a PDMS-derived layer, since PDMS contains a siloxane backbone and methyl groups bound to silicon. The nominal PDMS stoichiometry (C:Si:O = 2:1:1) explains the observed increase in carbon and silicon together with the relative decrease in oxygen compared with the native oxidized alloy surface.

This interpretation is further supported by the PM-IRRAS spectra, where characteristic PDMS-related CH₃ stretching, Si–CH₃ bending, and Si–O–Si vibrations were detected. In addition, previous work by Teisala et al. suggested that adventitious carbon can be replaced by PDMS during the grafting process.⁴⁴ This supports the assignment of the increased C1s contribution mainly to PDMS-derived methyl groups rather than to unspecific carbon contamination.

The combined SiO_x-CVD+PDMS modification exhibits the highest silicon and carbon contents among the investigated surface states. The C1s contribution increases to 22.4 at%, while the Si2p contribution reaches 20.5 at%. At the same time, the Al2p contribution decreases to 17.5 at%. The O1s contribution remains in the range of 39.1 at%. This combination of increased C1s and Si2p contents with reduced Al2p intensity strongly indicates the coexistence of the SiO_x-CVD interlayer and the PDMS-derived top layer. The reduced Al signal is consistent with attenuation of the alloy substrate by the deposited ultrathin film architecture, while the elevated Si content reflects contributions from the native Si-containing alloy surface, the SiO_x-CVD layer, and the PDMS-derived siloxane structure.

Together with the PM-IRRAS results, the XPS survey quantification therefore confirms the successful formation of the individual SiO_x-CVD and PDMS modifications as well as the combined SiO_x-CVD+PDMS thin-film architecture. In the next step, water contact angle measurements are used to evaluate how these chemical modifications affect the macroscopic wetting behavior of the polished and etched AM AlSi10Mg surfaces.

The water contact angle values obtained for the investigated surface states are summarized in Table 12 and exemplary photographs of a water droplet on each surface modification state is shown in Figure S8 in the Supporting Information. Both PDMS-containing surfaces show a pronounced increase in contact angle, independent of whether PDMS was grafted directly onto the aluminum oxide-terminated Reference surface or onto the SiO_x-CVD interlayer. This confirms the formation of hydrophobic PDMS-derived surface layers and is consistent with literature values reported for PDMS coatings.^{44,46} In contrast, the oxide-terminated surfaces, namely the Reference and SiO_x-CVD surface states, remain hydrophilic, with contact angles below 90°. The lower contact angle of the SiO_x-CVD surface compared with the Reference surface is attributed to the high surface hydroxyl density of the SiO_x film.

Table 12. Water contact angle values of the investigated surface states on polished and etched AM AlSi10Mg. Values are given as mean ± standard deviation. Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

Surface modification state	Water contact angle in °
Reference	51.7 ± 3.4
SiO _x -CVD	26.3 ± 5.0
PDMS	131.6 ± 6.2
SiO _x -CVD+PDMS	129.7 ± 1.6

Taken together, PM-IRRAS, XPS survey quantification, and WCA measurements confirm the successful formation of the applied surface modifications. While these results demonstrate the expected chemical and wettability changes, they do not provide detailed information on the chemical states and thicknesses of the native oxide and deposited ultrathin films. Therefore, the following section evaluates high-resolution Al2p and Si2p spectra to resolve the oxide-related contributions and to estimate the thickness of the native and applied thin-film layers.

4.2.4. XPS-based analysis of native oxide and thin-film thickness

The corrosion behavior of AlSi10Mg under atmospheric and chloride-containing conditions is strongly influenced by the chemical composition, electronic properties, and thickness of the native passive film. This is particularly relevant for LPBF-manufactured AlSi10Mg, where the polished and etched surface consists of an Al-rich matrix and Si-enriched eutectic regions, as shown in Section 4.2.2. These microstructural regions are expected to form chemically different oxide layers. While Al-rich areas are mainly covered by aluminum oxide/hydroxide species, the Si-enriched AlSi regions may form mixed Al–Si oxide or Si-containing oxide structures. The SKPFM results discussed in Section 4.2.2 further showed local Volta-potential differences between these microstructural regions, indicating that the Al-rich matrix and Si-enriched eutectic areas differ in their surface electronic properties. Although these measurements do not directly represent electrochemical activity in an electrolyte, they support the assumption that the heterogeneous Al–Si microstructure may promote local differences in interfacial reactivity once an electrolyte film is present.

In order to obtain a more detailed understanding of the native oxide structure and the subsequently applied ultrathin modifications, high-resolution XPS spectra of the Al2p and Si2p regions were evaluated. The analysis was used first to estimate the thickness of the native oxide layers on the Reference surface and subsequently to approximate the thicknesses of the SiO_x-CVD, PDMS, and SiO_x-CVD+PDMS thin films. It should be emphasized that this approach is based on a simplified model of a chemically and microstructurally heterogeneous surface. Therefore, the calculated values should be interpreted as estimated thickness ranges rather than exact film thicknesses.

The oxide thickness is calculated by using eq.(2-32). The peak areas I_o and I_m are obtained from component fits of the Al2p and Si2p spectra. To apply the thickness model, assumptions regarding the chemical composition of the oxide layers are required in order to define the corresponding atomic volume densities and inelastic mean free paths (i.e. N_o and λ_o , respectively). These assumptions were derived from the binding-energy positions (BE) of the fitted oxide components, as discussed in the following.

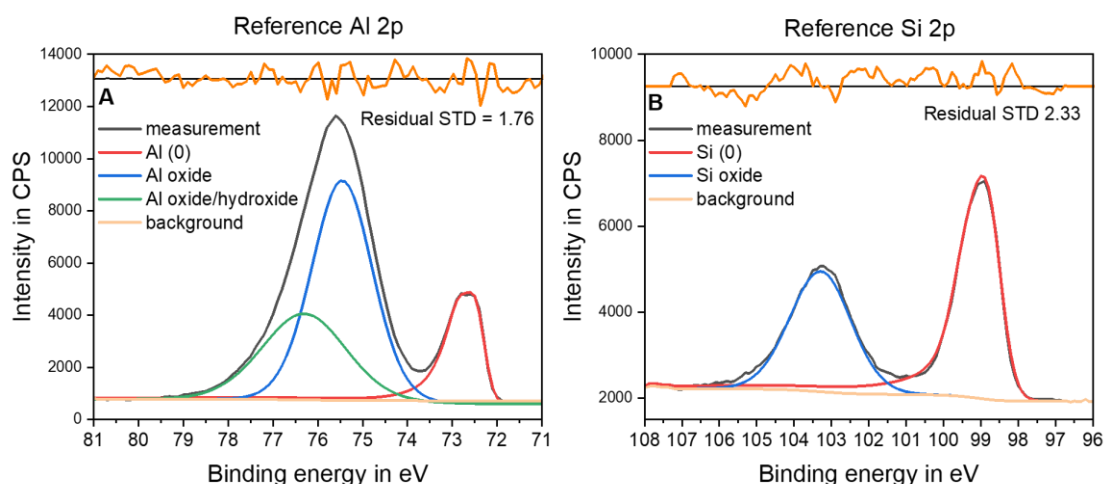


Figure 41. Al2p and Si2p HR-XPS spectra of polished, etched, and O₂-plasma-treated AM AlSi10Mg. (A) Al2p and (B) Si2p core-level spectra with component fits used to separate metallic and oxidized contributions. The residual standard deviation ("Residual STD") is included to indicate the fit quality. For clarity, spin-orbit split components assigned to the same chemical species are shown as combined contributions. Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, *Materials and Corrosion*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

The Al2p and Si2p core-level spectra of the Reference surface are shown in Figure 41. The Al2p spectrum was fitted using three contributions. The first component at a binding energy of 72.5 eV is assigned to metallic aluminum (Al(0)). A second component at 75.3 eV is attributed to Al₂O₃, while a third contribution at 76.2 eV is assigned to aluminum oxide/hydroxide species.¹⁵⁰ The Si2p spectrum was deconvoluted into a metallic Si contribution at 98.8 eV and an oxidized Si component at 103.1 eV, which is associated with the native oxide formed on Si-containing regions of the AlSi10Mg surface.^{96,98}

The assignment of the oxide-related components is complicated by possible differential charging of thin oxide regions on the metallic alloy substrate. This effect is particularly relevant for XPS analysis of thin native oxides, because the metallic components and the insulating oxide contributions may not experience identical charging behavior. Consequently, the apparent binding energies of oxide species can be shifted to higher values, while the metallic components remain less affected.^{173,174,187} This makes a direct chemical assignment based only on the measured binding-energy positions difficult.

In order to obtain a first approximation of the oxide chemistry, the AdC contribution was used as an internal reference for the oxide-related signals. Although AdC referencing does not necessarily yield the true binding energy (BE) positions of the associated compounds,^{188,189} it remains a widely used approach in XPS analysis. Therefore, applying the C1s correction provides a pragmatic basis for comparing the obtained oxide binding energies with literature values, as long as the limitations of this referencing method are considered. Original BE positions and their spectral course are shown in Figure S9 in the Supporting Information. The C1s contribution attributed to AdC was detected at 285.8 eV. By shifting this value to a reference position of 284.8 eV^{46,96,98} and applying the resulting correction to the oxide components, corrected binding energies of 74.3 eV for the Al2p oxide contribution and 102.1 eV for the Si2p oxide contribution are obtained. These corrected values are in good agreement with reported values for similar AlSi10Mg alloy surfaces.^{96,98}

For Al2p, the corrected oxide BE position can be assigned to Al_2O_3 .¹⁷³ For Si2p, the interpretation is less straightforward, because the Si-rich regions in LPBF-manufactured AlSi10Mg are assumed to be not pure silicon phases but part of a mixed Al–Si eutectic microstructure. Therefore, the oxide formed on these regions may not correspond to pure SiO_2 , but may instead contain Al–Si oxide or suboxide contributions. Since the corrected Si2p oxide binding energy of 102.1 eV is lower than the characteristic value expected for SiO_2 (103.3 eV¹⁹⁰), kyanite (≈ 102.5 eV¹⁹¹) was used as an approximate model compound for the oxide on the Si-enriched AlSi regions in the subsequent thickness estimation. However, this assignment should be regarded as a simplified approximation, since the exact chemical state of silicon in the near-surface eutectic regions cannot be resolved unambiguously from the present XPS data alone.

Based on these assignments, the required parameters for the thickness calculation according to eq. (2-32) were selected and shown in Table 13. The required IMFP values, except for Al and Al-oxide, were calculated using the TPP-2M model from NIST database.¹⁹² For the aluminum-rich regions, an Al/ Al_2O_3 system was assumed. For the Si-containing regions, the oxide thickness was estimated using either kyanite or SiO_2 as limiting model materials. The calculated thickness of the native aluminum oxide layer is approximately 3.5 nm, which is consistent with reported native oxide thicknesses for comparable AlSi10Mg surfaces. For the oxide on the Si-containing regions, the estimated thickness depends on the assumed oxide composition and ranges from approximately 1.9 nm for pure SiO_2 to 2.5 nm when kyanite is used as model material.

These results suggest that the native oxide structure on the polished and etched AM AlSi10Mg surface is not uniform across the different microstructural regions. Within the simplified two-phase model used here, the Al-rich matrix is covered by an approximately 3.5 nm thick aluminum oxide layer, whereas the oxide associated with the Si-enriched AlSi regions is thinner, with an estimated thickness between 1.9 nm and 2.5 nm. A simplified model of the expected structure of the polished and etched AM AlSi10Mg surface is schematically presented in Figure 42. This difference in oxide thickness and composition may contribute to local variations in interfacial reactivity under corrosive conditions and may also have affected the Volta potential differences measured in Section 4.2.2.

However, it should be again mentioned, that the calculated values should not be interpreted as exact local oxide thicknesses. The XPS signal represents an area-averaged response from a heterogeneous surface consisting of Al-rich and Si-enriched regions with different oxide chemistries. In addition, local surface topography may influence the XPS results. As shown in Figure 39A1, the Al–Si phase protrudes from the Al-rich matrix by approximately 100 nm. Such height differences can lead to local variations in the effective photoelectron take-off angle and may therefore affect the relative intensities used for the thickness estimation, as indicated by eq.(2-31). In addition, assumptions regarding the oxide composition, density, and inelastic mean free paths directly affect the calculated thickness values. Nevertheless, the analysis provides a useful estimate of the native oxide structure and supports the conclusion that the polished and etched AlSi10Mg surface presents chemically distinct oxide environments for subsequent SiO_x -CVD deposition and PDMS grafting.

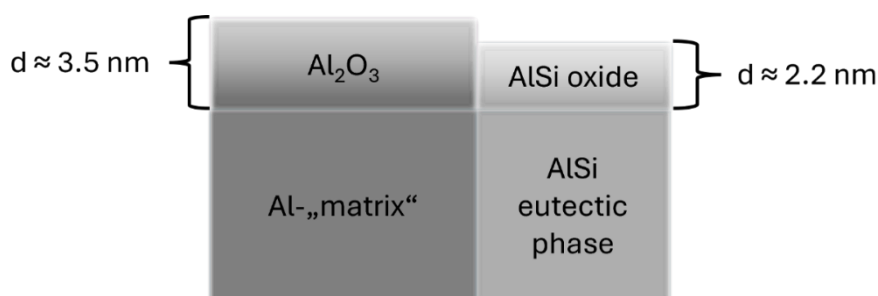


Figure 42. Simplified model of the native oxide structure on polished and etched AM AlSi10Mg. The schematic shows the assumed oxide configuration on Al-rich and Si-enriched regions of the heterogeneous alloy surface. The native oxide layer thicknesses d were estimated from HR-XPS data based on the model assumptions described in the text.

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Following the estimation of the native oxide thickness, the same XPS-based approach was applied to approximate the thicknesses of the deposited ultrathin films. This analysis is relevant because the electrochemical and corrosion-related behavior of the investigated surface states depends not only on the chemical nature of the modifications, but also on the thickness and continuity of the resulting interfacial layers. Since the SiO_x -CVD, PDMS, and SiO_x -CVD+PDMS modifications all contain silicon-based structures, the Si2p core-level spectra were used as the basis for the thickness estimation. Al2p spectra has been used to verify stable Al-oxide thickness values throughout the modification process.

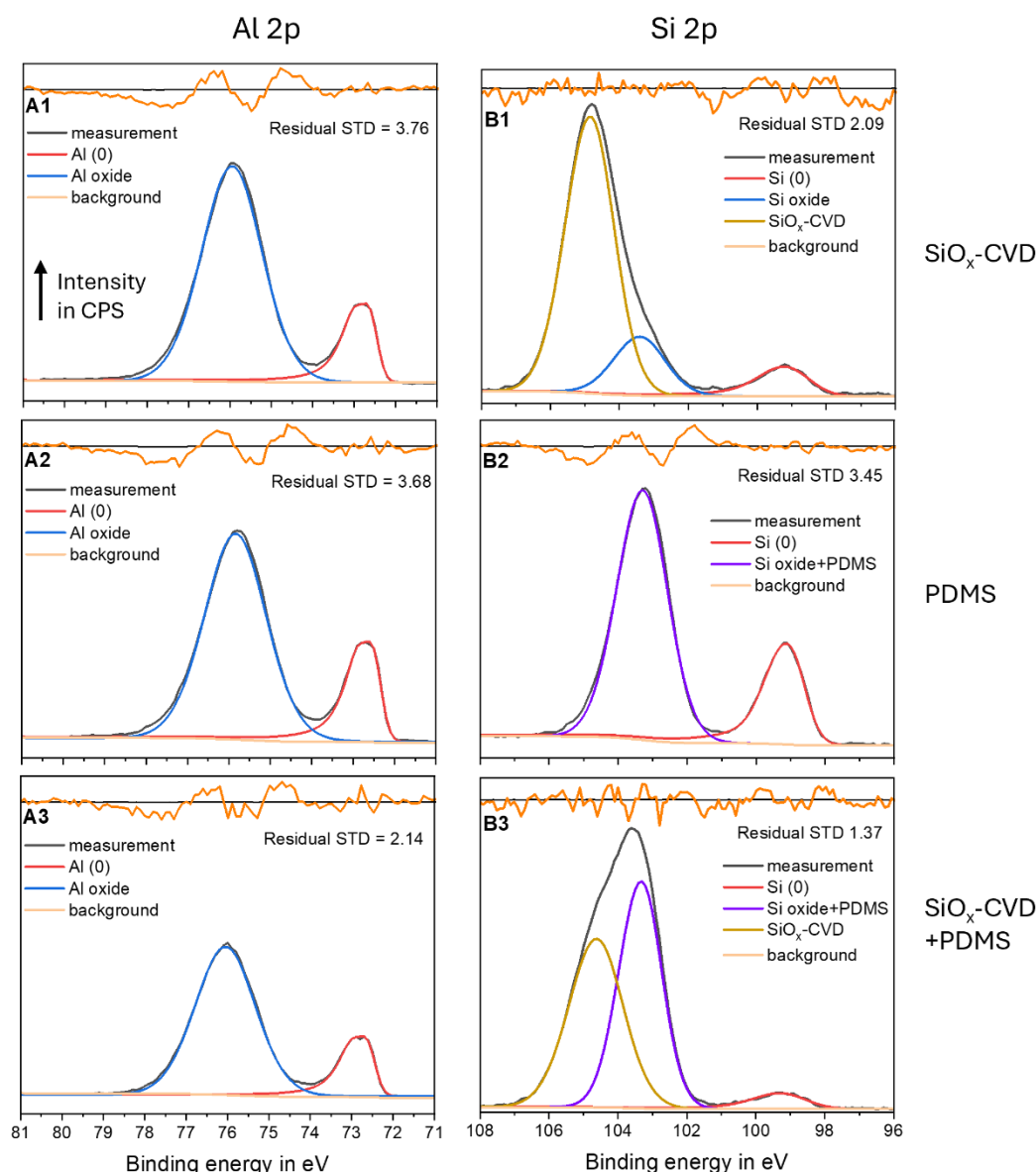


Figure 43. Al₂p and Si₂p HR-XPS spectra of thin-film-modified AM AlSi10Mg surfaces. Column A shows the Al₂p core-level spectra with corresponding component fits for SiO_x-CVD (A1), PDMS (A2), and SiO_x-CVD+PDMS (A3). Column B shows the corresponding Si₂p core-level spectra and component fits for SiO_x-CVD (B1), PDMS (B2), and SiO_x-CVD+PDMS (B3). The intensities of each core-level region are scaled equally to allow comparison between the different surface states. The residual standard deviation ("Residual STD") is included above each spectrum to indicate the quality of the fit. For clarity, spin-orbit split components assigned to the same chemical species are shown as combined contributions. Reproduced from: Pr  bner et al. (2026), "Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting", *Materials and Corrosion*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

The Al₂p and Si₂p core-level spectra of the modified surfaces are shown in Figure 43. For the SiO_x-CVD-modified surface, the Si₂p spectrum (Figure 43B1) was fitted using three components: metallic Si(0), native Si oxide, and an additional SiO_x-CVD-related contribution. The latter appears at an elevated binding energy with respect to the native Si oxide component, with a shift of $\Delta BE \approx 1.6$ eV. A comparable shift is observed in the corresponding O1s spectrum, where the SiO_x-CVD-related oxygen contribution is shifted by approximately $\Delta BE \approx 1.4$ eV relative to the native oxide contribution (see Figure S9). After C1s-based correction of the oxide-related components,

binding-energy values of 103.3 eV for the Si2p SiO_x-CVD contribution and 532.7 eV for the corresponding O1s contribution are obtained. These values are consistent with reported values for SiO_x/SiO₂-like materials and support the assignment of the additional Si2p component to the deposited SiO_x-CVD layer.^{138,171,190} This interpretation is further corroborated by the PM-IRRAS results, which showed characteristic Si–O–Si absorption bands for the SiO_x-CVD modification.

For the directly PDMS-modified surface, the Si2p spectrum was fitted using only two components (see Figure 43B2). A separate PDMS-related Si2p contribution could not be clearly distinguished from the native Si oxide contribution because both signals overlap in a similar BE region. Therefore, the PDMS-related silicon signal cannot be resolved unambiguously by component fitting alone. However, this observation is important to highlight, since it means that there is no additional charging upon applying a PDMS layer, which means that the system is still in a sufficient electrical contact with the ground. Nevertheless, the presence of PDMS is supported by the XPS survey quantification and by the characteristic PDMS absorption bands observed in PM-IRRAS. In contrast, the Si2p spectrum of the SiO_x-CVD+PDMS surface could again be deconvoluted into three components, analogous to the SiO_x-CVD-modified surface, indicating the presence of an additional silicon-containing overlayer contribution in the combined thin-film architecture. All applied fit parameters for Si2p and Al2p spectra are summarized in Table S2 and Table S3, respectively.

For the thickness estimation, the same attenuation-based approach as described above was applied to the Si2p spectra. In the case of the SiO_x-CVD layer, the total oxide thickness was first calculated by assuming either amorphous SiO₂ or kyanite as model material for the oxide. Subsequently, the previously estimated native oxide thickness ($d_{\text{d.o.}}$) of the Si-containing regions was subtracted from this total thickness (d_{total}) to obtain the effective SiO_x-CVD film thickness. This procedure yields a SiO_x-CVD layer thickness in the range of approximately 3.5–4.0 nm.

The same approach was applied to the directly grafted PDMS layer. Since the PDMS-related Si2p contribution could not be separated clearly from the native Si oxide component, the thickness was estimated using limiting assumptions, considering either PDMS or kyanite as model overlayer materials. Depending on the selected model material, the calculated PDMS film thickness lies between approximately 2.0 nm and 3.2 nm.

For the combined SiO_x-CVD+PDMS modification, the total film thickness was estimated by considering different silicon-containing model materials, namely kyanite, amorphous SiO₂, and PDMS. This results in a calculated thickness range of approximately 4.9–6.8 nm for the combined bilayer system. The larger thickness compared with the individual SiO_x-CVD and PDMS modifications is consistent with the coexistence of the inorganic SiO_x-CVD interlayer and the PDMS-derived top layer.

Overall, the calculated thickness ranges are in good agreement with the nanometer-scale film thicknesses reported for room-temperature PDMS grafting on SiO_x-containing surfaces.⁴⁴ The comparable BE positions observed for all modified surface states indicate that the ultrathin SiO_x-CVD, PDMS, and SiO_x-CVD+PDMS layers do not induce pronounced additional differential charging during XPS analysis. This suggests that the films remain sufficiently thin and/or sufficiently coupled to the conductive alloy substrate to maintain adequate electrical contact with the grounded sample holder. This distinction is important for the subsequent electrochemical interpretation, because the corrosion-related effect of these modifications is expected to arise from changes in interfacial chemistry, wettability, and charge-/ion-transfer resistance rather than from a thick, physically blocking barrier layer.

Table 13. Parameters used for the XPS-based oxide and film thickness estimations and resulting calculated thickness values. I_m and I_o denote the peak areas of the metallic and oxidized photoelectron contributions, respectively. N_m and N_o are the corresponding atomic volume densities of the analyzed element in the metallic and oxidized states, while λ_m and λ_o represent the inelastic mean free paths of the photoelectrons in the metal and oxide. d_{total} describes the total calculated thickness, including the native oxide and, where applicable, the applied ultrathin film. For aluminum oxide, d_{total} corresponds to the native oxide thickness. The film thickness d_{film} was calculated as $d_{total} - d_{native\ oxide}$. The thickness determination of aluminum oxide was based on the approach and parameters reported by Strohmeier.¹⁵⁰ All other values were obtained using the NIST Electron Inelastic-Mean-Free-Path Database.¹⁹² Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

Element	Surface modification state	Formula (metal/oxide)	I_o in at%	I_m in at%	λ_o in nm	λ_m in nm	N_o	N_m	d_{total} in nm	d_{film} in nm
Al 2p	Reference	Al/Al _{ox}	88.8	11.2	2.8	2.6	1.0	1.5	3.5	-
	SiO _x -CVD	Al/Al _{ox}	88.6	11.4	2.8	2.6	1.0	1.5	3.5	-
	PDMS	Al/Al _{ox}	85.5	14.5	2.8	2.6	1.0	1.5	3.1	-
	SiO _x -CVD+PDMS	Al/Al _{ox}	87.4	12.6	2.8	2.6	1.0	1.5	3.3	-
Si 2p	Reference	(Al)Si/Al ₂ SiO ₅	48.8	51.2	3.6	3.0	1.0	3.7	2.5	-
	SiO _x -CVD	(Al)Si/SiO ₂	92.3	7.7	3.9	3.0	1.0	2.3	6.0	3.5
		(Al)Si/Al ₂ SiO ₅	92.3	7.7	3.6	3.0	1.0	3.7	6.5	4.0
	PDMS	(Al)Si/PDMS	78.2	21.8	3.9	3.0	1.0	6.3	5.7	3.2
		(Al)Si/Al ₂ SiO ₅	78.2	21.8	3.6	3.0	1.0	3.7	4.5	2.0
	SiO _x -CVD+PDMS	(Al)Si/SiO ₂	96.1	3.9	3.9	3.0	1.0	2.3	7.4	4.9
		(Al)Si/PDMS	96.1	3.9	3.9	3.0	1.0	6.3	9.3	6.8
		(Al)Si/Al ₂ SiO ₅	96.1	3.9	3.6	3.0	1.0	3.7	7.8	5.3

The parameters used for the XPS-based thickness estimations, together with the resulting calculated thickness values, are summarized in Table 13 and schematically illustrated in Figure 44. The input parameters used for the IMFP calculations of kyanite and PDMS are provided in Table S4 in the Supporting Information.

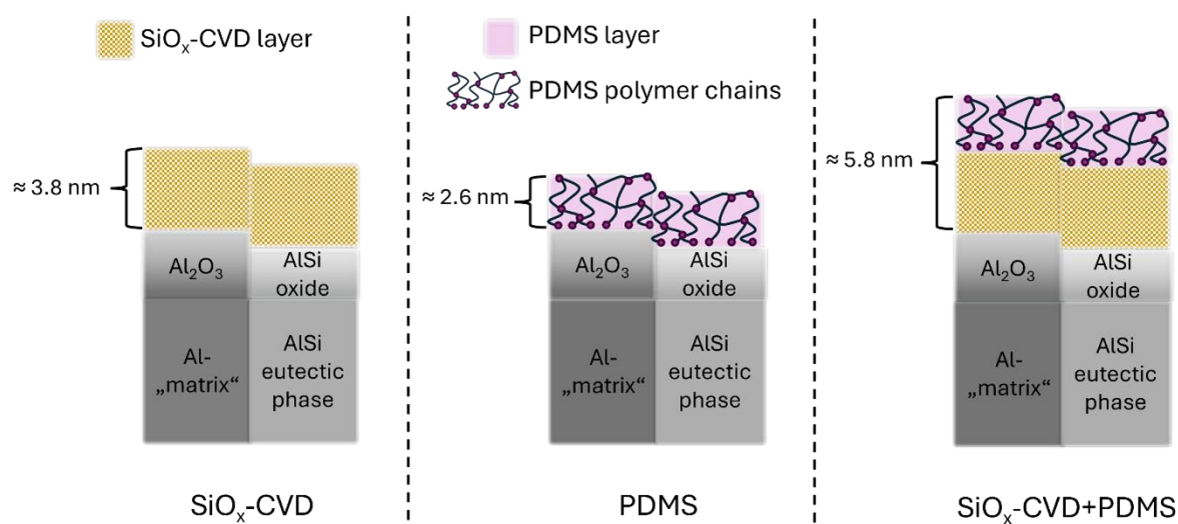


Figure 44. Schematic representation of the XPS-based film thickness estimates for the investigated surface modifications. The schematic summarizes the average calculated thicknesses derived from eq. (2-32) for the individual $\text{SiO}_x\text{-CVD}$ and PDMS modifications as well as for the combined $\text{SiO}_x\text{-CVD+PDMS}$ thin-film architecture. The left panel shows the estimated thickness of the $\text{SiO}_x\text{-CVD}$ layer, the center panel shows the estimated thickness of the PDMS-derived layer and schematically illustrates the partially cross-linked polymeric network, and the right panel shows the estimated total thickness of the $\text{SiO}_x\text{-CVD+PDMS}$ bilayer. The values represent model-based thickness estimates rather than exact local layer thicknesses. Reproduced from: Prübner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining $\text{SiO}_x\text{-CVD}$ and PDMS Grafting“, *Materials and Corrosion*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

4.2.5. Electrochemical performance of $\text{SiO}_x\text{-CVD/PDMS}$ thin-film architectures

After confirming the successful formation of the $\text{SiO}_x\text{-CVD}$, PDMS, and $\text{SiO}_x\text{-CVD+PDMS}$ thin-film architectures, their electrochemical behavior was evaluated in chloride-containing electrolyte. The aim of this section is to determine whether the spectroscopically verified ultrathin modifications also affect the electrochemical response of the Reference surface. For this purpose, electrochemical impedance spectroscopy, linear sweep voltammetry, and chronoamperometry were applied using the droplet-cell setup. This approach allows the influence of the individual $\text{SiO}_x\text{-CVD}$ and PDMS layers, as well as their combined architecture, to be assessed with respect to barrier properties, charge-transfer resistance, corrosion current density, and pitting tendency.

Representative EIS spectra of the investigated surface states are shown in Figure 45A1. The low-frequency impedance increases for all modified surfaces compared with the Reference, indicating improved resistance against electrolyte-induced interfacial processes. This demonstrates that even nanometer-scale $\text{SiO}_x\text{-CVD}$ and PDMS-based films can significantly alter the electrochemical response of the polished and etched AM AlSi10Mg surface. The increase in impedance is consistent with the previously discussed XPS- and PM-IRRAS-based evidence for thin-film formation and with the reduced surface wettability of the PDMS-containing modifications.

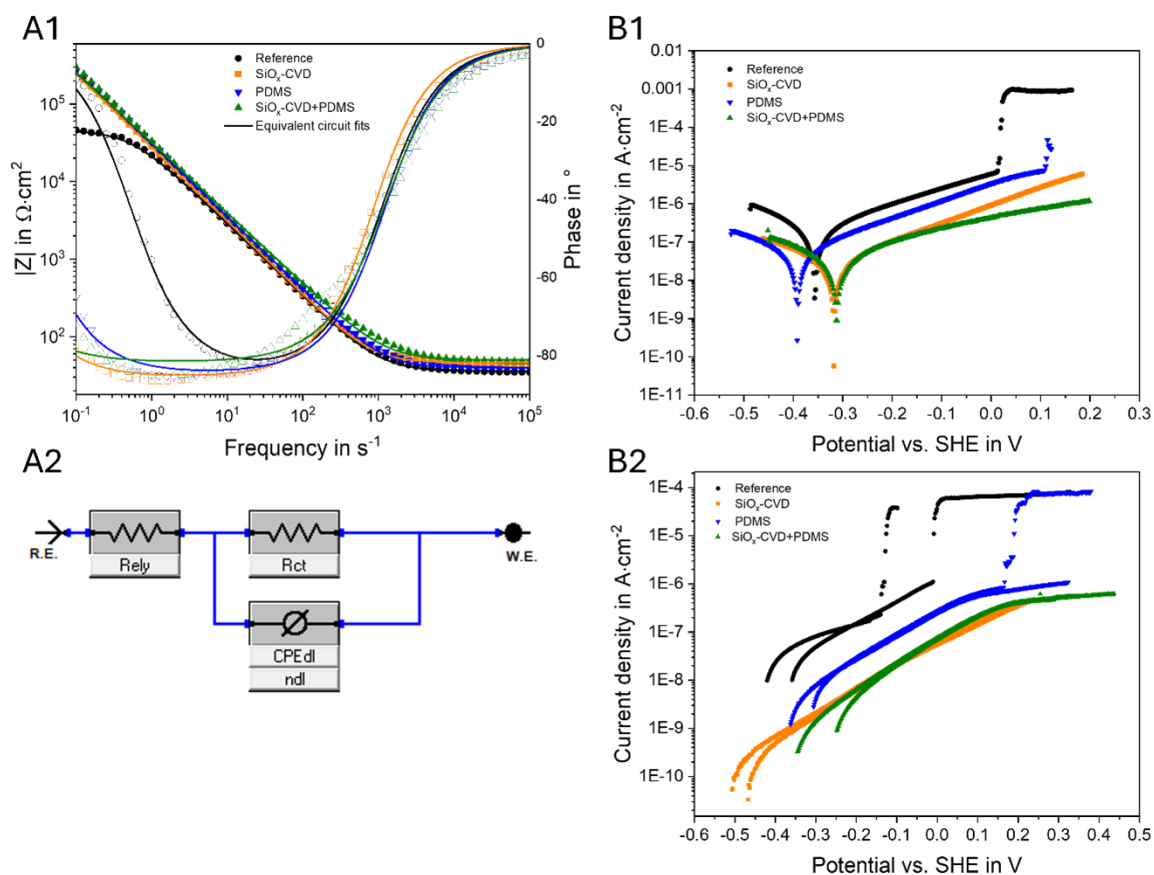


Figure 45. Representative EIS and LSV results of the investigated surface states. Column A presents representative EIS spectra of the different surface modifications (A1) together with the corresponding equivalent-circuit fit results. The equivalent circuit used for fitting is shown in (A2). Column B shows representative LSV curves recorded after cathodic pre-polarization (B1) and during purely anodic polarization (B2). Reproduced from: Prübner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining $\text{SiO}_x\text{-CVD}$ and PDMS Grafting“, *Materials and Corrosion*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

To obtain a more quantitative interpretation of the impedance response, the EIS spectra were fitted using a modified Randles-type equivalent circuit. This model was selected because the Nyquist and Bode representations showed only one clearly distinguishable time constant under the applied measurement conditions. In line with the fitting strategy used in Section 4.1.6, the simplest equivalent circuit that adequately described the electrochemical response was chosen. Accordingly, the ultrathin surface films were not treated as independent thick coating layers, but rather as part of the interfacial region that modifies charge transfer and non-ideal capacitive behavior at the alloy/electrolyte interface. The equivalent circuit consists of the electrolyte resistance R_{ely} in series with a parallel combination of the charge-transfer resistance R_{ct} and a constant phase element CPE_{dl} , which accounts for the non-ideal capacitive behavior of the electrochemical double layer. Additionally, C_{eff} has been calculated by eq. (2-46).

Table 14. Equivalent-circuit fitting results for the electrochemical characterization of the investigated surface states. The parameters were obtained from fits of the EIS spectra (Figure 45A1) using the equivalent circuit shown in Figure 45A2. Values are reported as mean $\pm$ standard deviation. Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

Surface state	$R_{ely}/\Omega \cdot \text{cm}^2$	$R_{ct}/\text{M}\Omega \cdot \text{cm}^2$	$Q_{CPE,dl}/\mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$	n_{dl}	$\chi^2 \cdot 10^{-3}$	$C_{eff}/\mu\text{F} \cdot \text{cm}^{-2}$
Reference	39.9 $\pm$ 5	0.12 $\pm$ 0.06	6.4 $\pm$ 0.4	0.94 $\pm$ 0.004	1.8 $\pm$ 0.3	3.8 $\pm$ 0.1
SiO _x -CVD	40.1 $\pm$ 5	3.11 $\pm$ 0.46	6.2 $\pm$ 0.01	0.95 $\pm$ 0.001	2.3 $\pm$ 0.3	4.0 $\pm$ 0.1
PDMS	45.3 $\pm$ 4	0.73 $\pm$ 0.23	5.1 $\pm$ 0.5	0.94 $\pm$ 0.002	2.8 $\pm$ 0.2	3.0 $\pm$ 0.3
SiO _x -CVD +PDMS	61.9 $\pm$ 12	3.81 $\pm$ 1.23	5.3 $\pm$ 0.5	0.92 $\pm$ 0.02	7.8 $\pm$ 1.7	2.7 $\pm$ 0.2

The fit parameters summarized in Table 14 confirm the beneficial influence of the applied surface modifications. The Reference surface exhibits a comparatively low charge-transfer resistance of $0.12 \text{ M}\Omega \cdot \text{cm}^2$. After SiO_x-CVD deposition, R_{ct} increases significantly to $3.11 \text{ M}\Omega \cdot \text{cm}^2$, indicating that the inorganic SiO_x-CVD interlayer effectively suppresses interfacial charge-transfer processes. The directly PDMS-modified surface also shows an increased R_{ct} of $0.73 \text{ M}\Omega \cdot \text{cm}^2$, although the effect is less pronounced than for the SiO_x-CVD-modified surface. The combined SiO_x-CVD+PDMS architecture yields the highest charge-transfer resistance of $3.81 \text{ M}\Omega \cdot \text{cm}^2$, suggesting that the bilayer combines the beneficial effects of the inorganic interlayer and the hydrophobic PDMS top layer.

The fitted capacitive response further differentiates the influence of the individual modifications. The effective capacitance C_{eff} , derived from the CPE parameters using eq. (2-46), is $3.8 \mu\text{F} \cdot \text{cm}^{-2}$ for the Reference and remains similar for the SiO_x-CVD surface with $4.0 \mu\text{F} \cdot \text{cm}^{-2}$. In contrast, PDMS modification reduces C_{eff} to $3.0 \mu\text{F} \cdot \text{cm}^{-2}$, and the combined SiO_x-CVD+PDMS modification further decreases it to $2.7 \mu\text{F} \cdot \text{cm}^{-2}$. This decrease indicates a modification of the interfacial dielectric properties and/or an increase in the effective thickness of the electrochemical interphase after PDMS grafting. Thus, while the SiO_x-CVD layer primarily increases the charge-transfer resistance, PDMS mainly affects the capacitive response of the interface.

Overall, the EIS results indicate that the individual thin films influence different aspects of the electrochemical response. The SiO_x-CVD layer predominantly increases R_{ct} , suggesting reduced interfacial electron-transfer activity. The PDMS layer has a more pronounced effect on the capacitive behavior, consistent with the formation of a hydrophobic, low-surface-energy organic interphase. When both modifications are combined, these effects are superimposed, resulting in the highest R_{ct} and the lowest C_{eff} among the investigated surface states.

To further assess the corrosion-related behavior of the investigated surface states, linear sweep voltammetry was performed. In contrast to EIS, which probes the impedance response under small-amplitude perturbation, LSV provides information on the current response during controlled polarization and allows the onset of passive film breakdown or localized corrosion to be evaluated. The resulting polarization curves were used to evaluate characteristic corrosion parameters by Tafel analysis, as described in Section 2.4.3.2.

Representative results are shown in Figure 45B1 and the extracted Tafel parameters are summarized in Table 15.

Table 15. Tafel-plot parameters derived from LSV measurements of the Reference and thin-film-modified AM AlSi10Mg surfaces. The corrosion potential E_{corr} , corrosion current density i_{corr} , and anodic and cathodic Tafel slopes b_a and b_c were obtained from the polarization curves shown in Figure 45_B1. Values are given as mean $\pm$ standard deviation.

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Surface state	E_{corr} in mV vs SHE	i_{corr} in $\mu\text{A} \cdot \text{cm}^{-2}$	b_a in $\text{mV} \cdot \text{dec}^{-1}$	b_c in $\text{mV} \cdot \text{dec}^{-1}$
Reference	-349 ± 30	0.28 ± 0.18	209.9 ± 58.7	-143.9 ± 40.3
SiO _x -CVD	-324 ± 50	0.02 ± 0.01	219.6 ± 32.1	-240.4 ± 58.4
PDMS	-408 ± 40	0.06 ± 0.03	209.3 ± 23.4	-253.3 ± 34.4
SiO _x -CVD +PDMS	-329 ± 50	0.04 ± 0.02	236.2 ± 27.2	-208.2 ± 27.4

The corrosion current densities i_{corr} obtained from the Tafel analysis follow the same general trend as the charge-transfer resistances derived from the EIS fits and are consistent with other published values for polished and etched AM AlSi10Mg surfaces.^{99,193} The Reference surface exhibits the highest corrosion current density of $0.28 \mu\text{A} \cdot \text{cm}^{-2}$. All modified surfaces show distinctly lower values by approximately one order of magnitude, indicating that the applied thin films reduce the overall corrosion kinetics under the investigated conditions.

The corrosion potentials E_{corr} show smaller but still relevant differences between the surface states. The Reference surface exhibits an E_{corr} of -349 mV vs. SHE. After SiO_x-CVD deposition and SiO_x-CVD+PDMS modification, the corrosion potentials shift slightly in the anodic direction to -324 mV vs. SHE and -329 mV vs. SHE, respectively. In contrast, the directly PDMS-modified surface shows a more cathodic corrosion potential of -408 mV vs. SHE. This indicates that the individual surface modifications might not affect the anodic and cathodic partial reactions in the same way.

The Tafel slopes provide further insight into the kinetic influence of the surface modifications. For the Reference surface, the anodic Tafel slope b_a is $209.9 \text{ mV dec}^{-1}$, whereas the cathodic slope b_c is $-143.9 \text{ mV dec}^{-1}$. The comparatively lower absolute value of b_c indicates a more pronounced cathodic activity for the Reference surface. This behavior can be related to the heterogeneous Al–Si microstructure discussed in Section 4.2.2. Si-enriched regions exhibit higher Volta potentials than the Al-rich matrix and may therefore act as comparatively noble sites, promoting cathodic reactions such as oxygen reduction when an electrolyte is present. As discussed in Sections 2.1.3.2 and 2.2.1.2, this can lead to pitting and/or trenching in the vicinity of cathodically active phases, which has also been reported in other studies.^{99,101,194}

However, after applying the surface modifications, the absolute cathodic Tafel slopes increase. The SiO_x-CVD, PDMS, and SiO_x-CVD+PDMS surfaces show b_c values of $-240.4 \text{ mV} \cdot \text{dec}^{-1}$, $-253.3 \text{ mV} \cdot \text{dec}^{-1}$, and $-208.2 \text{ mV} \cdot \text{dec}^{-1}$, respectively. These values are closer to, or even higher than, the corresponding anodic slopes. This suggests that the thin-film modifications reduce the cathodic activity of the alloy surface. Such an effect is consistent with the reduced corrosion current densities and supports the assumption that the coatings partly suppress electrolyte access to cathodically active Si-rich microstructural regions.

This interpretation of the Tafel parameters is further supported by the passive breakdown behavior observed in the LSV curves, particularly for the Reference surface (Figure 45B1). The Reference

surface shows a pronounced increase in current density at anodic potentials, which is most likely associated with the onset of localized corrosion or passive film breakdown. In contrast, the SiO_x-CVD-containing surfaces exhibit a more stable current response over the investigated potential range. The directly PDMS-modified surface still shows evidence of passive film breakdown, but the corresponding pitting-related current increase is shifted toward more anodic potentials compared with the Reference. This indicates that PDMS grafting can delay the onset of pitting, even though it does not suppress it as effectively as the SiO_x-containing modifications.

To evaluate the pitting behavior without the influence of cathodic pre-polarization, purely anodic polarization curves were additionally recorded, as shown in Figure 45B2. The trends are consistent with the measurements performed after cathodic pre-polarization. The Reference surface and the directly PDMS-modified surface exhibit passive film breakdown, whereas the PDMS-modified surface shows this breakdown at a more anodic potential. In contrast, the SiO_x-CVD and SiO_x-CVD+PDMS surface states do not show clear pitting within the investigated potential range. This confirms that the SiO_x-containing modifications are particularly effective in suppressing localized corrosion initiation during the short-term electrochemical measurements.

To further evaluate the stability of the investigated surface states under mild anodic polarization, chronoamperometric measurements were performed. By applying a constant potential of +0.1 V vs. OCP for 800 s, the electrochemical system was anodically perturbed and its current relaxation behavior was monitored over time. Since this polarization is substantially lower than the high anodic potentials reached during LSV measurements, the method provides a less aggressive approach for probing active and passive current development. It is therefore particularly useful for evaluating early-stage interfacial stability under conditions that are more relevant to thin-electrolyte-film exposure and atmospheric corrosion than to strongly forced anodic polarization in bulk electrolyte. The corresponding current transients are shown in Figure 46.

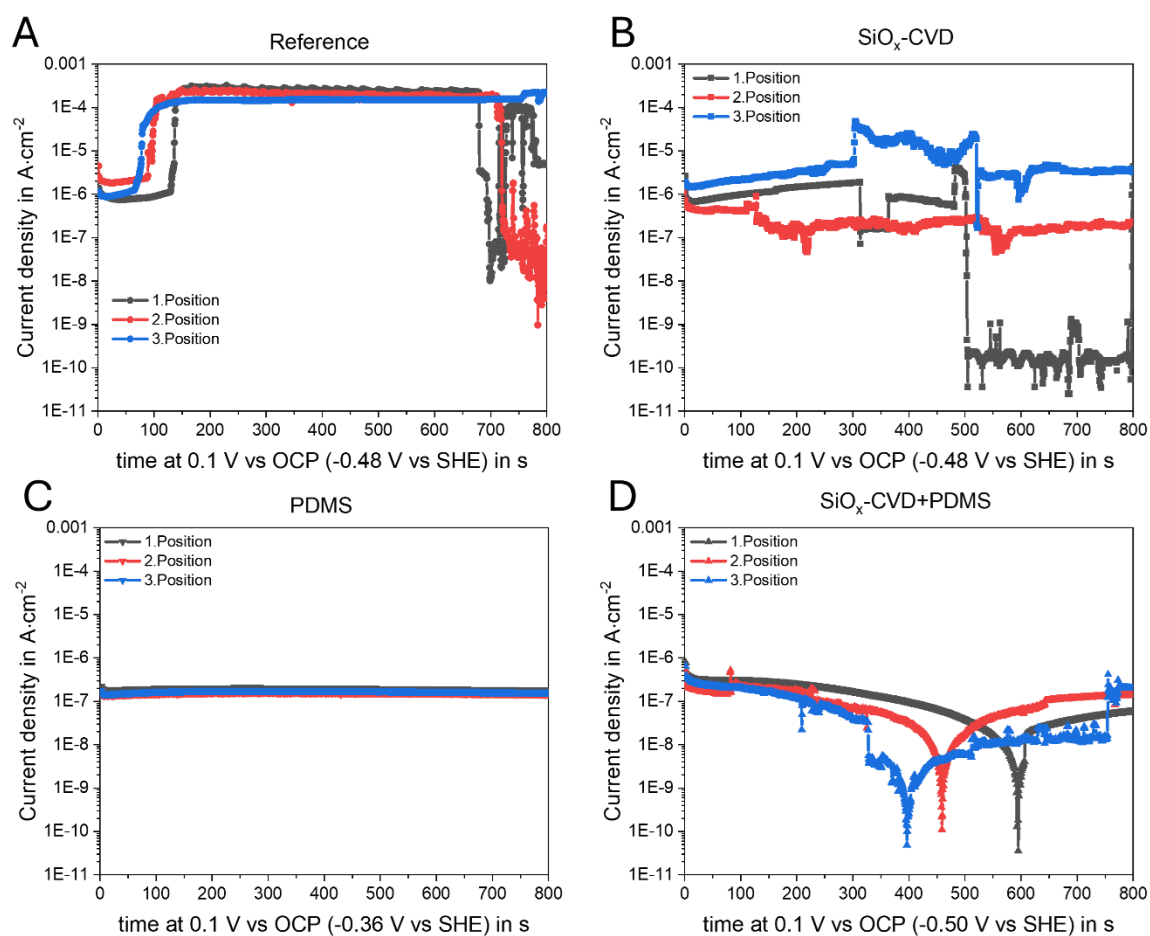


Figure 46. Chronoamperometric response of the investigated AM AlSi10Mg surface states under mild anodic polarization. Current density transients are shown for (A) Reference, (B) SiO_x-CVD, (C) PDMS, and (D) SiO_x-CVD+PDMS surfaces. The measurements were performed at a constant potential of +0.1 V vs. OCP, and the current density is plotted as a function of time. The OCP values given in brackets correspond to the mean OCP values of the measurements shown in the respective panels. Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, *Materials and Corrosion*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

When comparing the different surface states, it should be noted that the absolute OCP of the PDMS-modified surface is shifted by approximately 0.13 V toward more positive potentials compared with the other investigated surfaces. Since the chronoamperometric measurements were performed at +0.1 V vs. OCP, the PDMS-modified surface was effectively polarized at a more anodic absolute potential. This has to be considered when comparing absolute current densities. Nevertheless, the current-time response provides important qualitative information on the tendency toward passive film breakdown and localized corrosion.

The Reference surface shows the least stable current response. As shown in Figure 46A, all measurements exhibit a pronounced increase in current density during the first 200 s, reaching values comparable to the pitting-related current densities observed in the anodic LSV curves ($\approx 100 \mu\text{A} \cdot \text{cm}^{-2}$). This behavior indicates the onset of localized corrosion or passive film breakdown under the applied anodic polarization. In two of the three measurements, the current density decreases again after approximately 700 s, which may be associated with partial pit re-passivation.

For the SiO_x-CVD-modified surface (Figure 46B), the current density is generally reduced compared with the Reference, in agreement with the preceding EIS and LSV results. The pitting-related current densities are also lower than for the unmodified surface. Nevertheless, the occurrence of local current fluctuations indicates that the SiO_x-CVD layer does not completely suppress interfacial activity. Rather, the modification appears to reduce the severity of pitting-related processes and promotes lower, passivated current responses.

The directly PDMS-modified surface shows a particularly relevant behavior. Despite being measured at a more anodic absolute potential due to its shifted OCP, the current densities remain comparatively low and no pronounced pitting-related current rise is observed within the investigated time window. Consistent with the EIS results, this behavior may be associated with an increased effective capacitive layer thickness induced by the PDMS modification. Such an increase can retard ion transport to and from the surface. Based on the potential step experiments, the PDMS-modified surface therefore appears to mitigate passive layer breakdown and inhibit pitting-related processes.

The combined SiO_x-CVD+PDMS modification strongly suppresses abrupt pitting-related current transients. The observed low current densities and only gradual current increase indicate delayed electrolyte access and a stabilized passive interfacial state rather than immediate passive film breakdown. This indicates that the bilayer architecture combines the beneficial effects of both individual modifications: the SiO_x-CVD interlayer contributes to an increased charge-transfer resistance, while the hydrophobic PDMS top layer reduces electrolyte accessibility and stabilizes the interfacial response under anodic polarization.

Overall, the chronoamperometric measurements support the trends observed by EIS and LSV. The unmodified Reference surface is prone to rapid passive film breakdown under anodic polarization, whereas the thin-film-modified surfaces show reduced current densities and suppressed or delayed pitting-related current transients. The SiO_x-CVD+PDMS architecture exhibits the most stable current-time response in the potential step experiments, indicating that the combination of an inorganic SiO_x-CVD interlayer with a hydrophobic PDMS-derived top layer provides an effective short-term stabilization of the polished and etched AM AlSi10Mg surface.

4.2.6. Atmospheric corrosion behavior under NaCl deposition

After the short-term electrochemical response of the thin-film-modified surfaces had been evaluated in chloride-containing electrolyte, their corrosion behavior was further investigated under simulated atmospheric conditions. This step is particularly relevant because atmospheric corrosion is governed by thin electrolyte films, salt deliquescence, local electrolyte retention, and wetting behavior rather than by complete immersion in bulk electrolyte (see Section 2.1.4.3). For this purpose, the samples were loaded with a NaCl deposit of approximately 130 μg·cm⁻² and exposed for 36 days to a humid atmosphere of 75 ± 2 %r.h. at 20.5 ± 1 °C using the exposure cell shown in Figure 23.

After exposure, the Reference and SiO_x-CVD surfaces exhibited pronounced localized corrosion attacks, as shown in Figure 47. In both cases, residual NaCl crystals and corrosion products were strongly adhered to the surface after exposure and could not be completely removed by water immersion, even after several days. The digital microscopy images were evaluated using ImageJ in order to estimate the extent of localized corrosion. For the Reference surface, at least nine pitting events were identified, one of which was classified as severe pitting with a pitting area

larger than 0.05 mm^2 . The corresponding total pitting area was approximately 0.7 % of the analyzed surface. The SiO_x -CVD surface showed three severe and one minor pitting event, also resulting in a comparable relative pitting area of approximately 0.7 %.

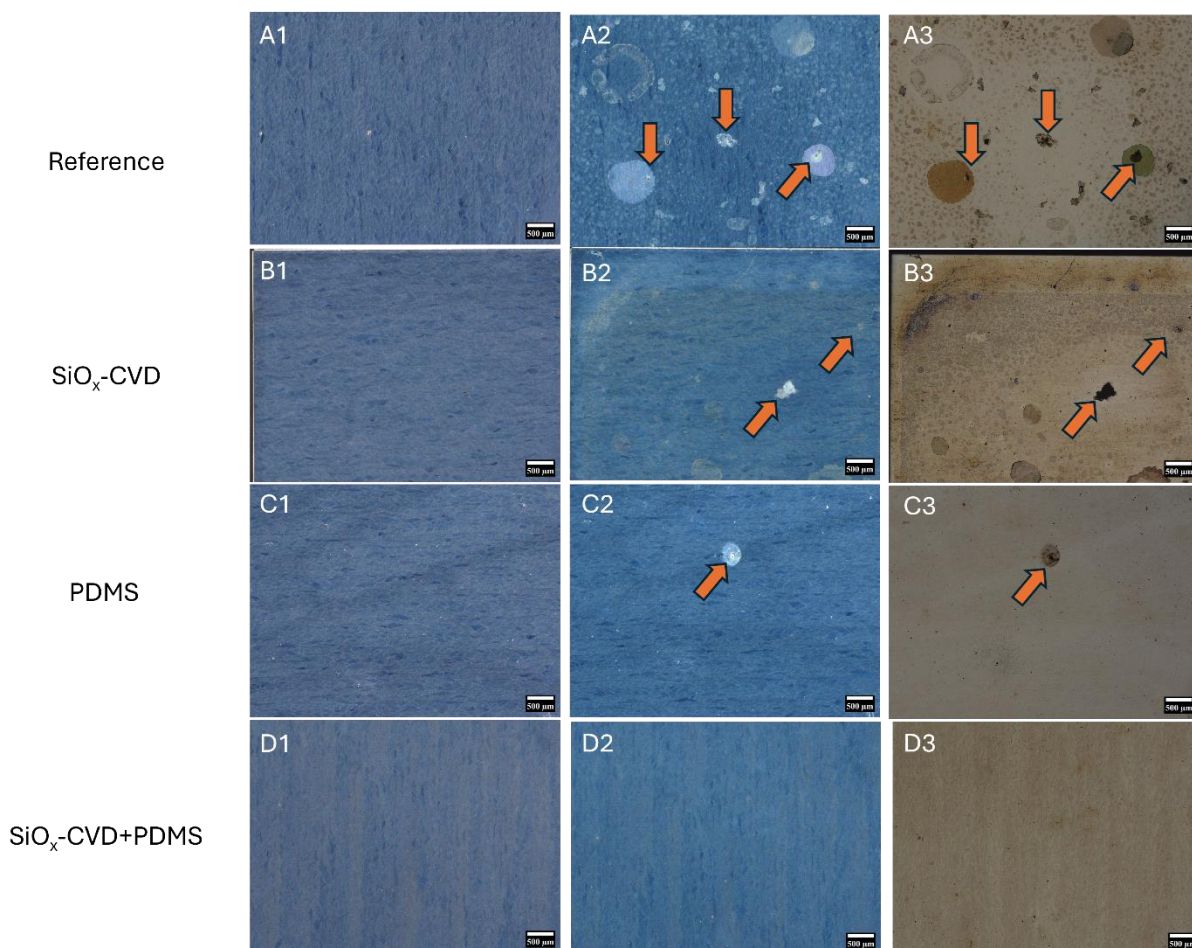


Figure 47. Digital microscopy images of NaCl-loaded AM AlSi10Mg surfaces before and after simulated atmospheric corrosion exposure. The samples were loaded with approximately $130 \mu\text{g} \cdot \text{cm}^{-2}$ NaCl and exposed to 75 % relative humidity for 36 days. Rows A–D correspond to the surface states Reference, SiO_x -CVD, PDMS, and SiO_x -CVD+PDMS, respectively. Images labeled 1 show the initial NaCl-loaded state before corrosive exposure, while images labeled 2 and 3 show the same surface positions after exposure using different illumination conditions. The scale bar in the bottom right corner of each image corresponds to 500 μm . Orange arrows indicate local corrosion events that were not present before exposure. Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x -CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

In addition to the localized pitting events, both the Reference and SiO_x -CVD surfaces showed broader areas affected by corrosion. However, a reliable quantitative determination of the total corroded area was limited by the low optical contrast between corroded and non-corroded regions in the digital microscopy images. Depending on the threshold selected for image analysis, the corroded area was estimated to be in the range of approximately 20–30 % for both surface states. Thus, the SiO_x -CVD layer alone did not provide sufficient protection under prolonged salt-contaminated atmospheric exposure, despite its favorable short-term electrochemical behavior discussed in Section 4.2.5.

In contrast, the PDMS-containing surface states showed markedly fewer corrosion sites. On the directly PDMS-modified surface, only one minor localized corrosion site with an area of approximately 0.01 mm^2 was detected. For the combined SiO_x -CVD+PDMS modification, no corrosion site was observed within the resolution of the digital microscopy analysis. A quantitative evaluation of the total corroded area was not feasible for the PDMS-containing surfaces because the contrast between potentially affected and unaffected regions was too low for reliable image segmentation. Nevertheless, the microscopy results clearly indicate that the presence of a PDMS-derived hydrophobic top layer strongly reduces the extent of atmospheric corrosion damage.

At first glance, these atmospheric corrosion results appear to differ from the short-term electrochemical measurements in bulk electrolyte, where the SiO_x -CVD surface showed very low corrosion current densities and high charge-transfer resistance. This apparent discrepancy can be explained by the fundamentally different corrosion conditions and protection mechanisms. Under complete immersion, the SiO_x -CVD layer can act as an electrochemically stabilizing interfacial layer and reduce charge-transfer processes, at least for short time intervals. Under atmospheric conditions, however, the hydrophilic character of the SiO_x -CVD surface favors electrolyte spreading and retention once the deposited NaCl becomes deliquescent. This facilitates the formation of continuous electrolyte pathways and may promote localized corrosion during prolonged exposure, despite favorable short-term electrochemical performance (see Section 2.1.4).

The PDMS-containing surfaces behave differently because their hydrophobic outer interface can reduce electrolyte wetting, limit the formation of continuous electrolyte films, and decrease the effective electrolyte/substrate contact area. Therefore, thin hydrophobic films do not necessarily act as classical thick barrier coatings or stable passive layers. Instead, their protective effect under atmospheric conditions is mainly associated with a reduction in effective time of wetness, restricted electrolyte spreading, and increased ionic transport resistance through reduced real contact area and possible air entrapment.^{47,88,195}

The superior performance of the SiO_x -CVD+PDMS modification can therefore be attributed to the combination of two complementary functions. The inorganic SiO_x -CVD interlayer contributes to the electrochemical stabilization of the interface, as indicated by the increased charge-transfer resistance in EIS, the reduced corrosion current densities obtained from LSV, and the suppressed pitting tendency observed in LSV and chronoamperometry. The hydrophobic PDMS top layer, in contrast, governs the wetting behavior under salt-contaminated atmospheric conditions and suppresses direct electrolyte–substrate interaction. This synergistic combination explains why the SiO_x -CVD+PDMS architecture provides the most effective protection under prolonged atmospheric exposure, whereas the individual SiO_x -CVD layer alone remains vulnerable due to electrolyte spreading and retention.

4.2.7. Conclusion on SiO_x /PDMS thin-film architectures

The aim of Section 4.2 was to evaluate whether PDMS can be attached to a more controlled, polished and etched AM AlSi10Mg surface and whether an additional SiO_x -CVD interlayer improves the resulting thin-film architecture. Compared with the as-built surface discussed in Section 4.1, polishing and etching provided a smoother and experimentally more accessible substrate. However, FE-SEM, EDS, AFM, and SKPFM showed that the surface remains locally heterogeneous, consisting of Al-rich matrix regions and Si-enriched eutectic structures with different topographical and Volta-potential characteristics. Thus, the pretreatment reduced

macroscopic roughness but preserved the intrinsic chemical and electronic heterogeneity of the LPBF-manufactured alloy.

The spectroscopic and wettability results demonstrate that PDMS can be successfully introduced onto the polished and etched AlSi10Mg surface even without an additional SiO_x-CVD adhesion layer. PM-IRRAS revealed characteristic PDMS-related CH₃, Si-CH₃, and Si-O-Si vibrational features, while XPS survey analysis showed increased C1s and Si2p contributions after PDMS modification. In addition, the water contact angle increased strongly to values above 130°, confirming the formation of a hydrophobic PDMS-derived outer surface. Therefore, the Si-containing AlSi10Mg surface appears to provide sufficient conditions for PDMS attachment under the applied room-temperature grafting procedure. However, the present data do not allow a definitive distinction whether the SiO_x-layer improves PDMS grafting/adhesion.

The role of the SiO_x-CVD interlayer is therefore not to enable PDMS attachment in an absolute sense, but rather to modify the chemical and functional properties of the resulting thin-film architecture. The SiO_x-CVD layer forms a hydrophilic, silicon oxide-rich interlayer with an estimated thickness in the nanometer range (3-4 nm). When combined with PDMS, the resulting SiO_x-CVD+PDMS architecture exhibits the highest Si2p and C1s contents, a hydrophobic outer surface, and, based on the simplified model introduced in Section 4.2.4, an increased total film thickness compared with the individual modifications. These results indicate that the SiO_x-CVD interlayer provides an additional silicon oxide-rich interface for PDMS attachment and contributes to the formation of a more complex bilayer-like architecture.

The electrochemical results further differentiate the functional contributions of the individual thin-film components. The SiO_x-CVD modification predominantly affects the resistive part of the impedance response. This is reflected by the strong increase in charge-transfer resistance and the reduced corrosion current densities obtained from LSV measurements. Thus, the SiO_x-CVD layer appears to stabilize the alloy/electrolyte interface against charge-transfer processes during short-term immersion-type measurements. However, the chronoamperometric experiments show that this stabilization is not equivalent to complete suppression of interfacial activity. The SiO_x-CVD surface still exhibits both active and passive current transients, indicating that local electrolyte access and transient activation of the AlSi10Mg surface are still possible.

The PDMS modification influences the electrochemical response in a different way. In EIS, PDMS mainly reduces the effective capacitance, which indicates a change in the dielectric properties and/or an increase in the effective capacitive layer thickness of the interface. This behavior is consistent with the formation of a hydrophobic organic layer that retards ion transport to and from the surface. In the chronoamperometric measurements, the directly PDMS-modified surface shows only passive current densities within the investigated time window, despite being polarized at a more anodic absolute potential due to its shifted OCP. This suggests that PDMS is particularly effective in delaying passive film breakdown and suppressing pitting-related current transients.

The SiO_x-CVD+PDMS bilayer combines these two contributions. In EIS, it exhibits both a high charge-transfer resistance and the lowest effective capacitance, indicating that the inorganic interlayer and the hydrophobic PDMS top layer affect complementary aspects of the electrochemical interface. This combined behavior is also reflected in the chronoamperometric response. The current densities are comparable to those of the PDMS-modified surface, but the transients reach particularly low current minima before increasing only gradually at longer polarization times. This behavior can be interpreted as delayed electrolyte availability caused by

the hydrophobic PDMS top layer, combined with a passivated interface provided by the SiO_x-CVD interlayer.

This differentiation is important for interpreting the atmospheric corrosion results. The SiO_x-CVD layer performs well in short-term electrochemical measurements in bulk electrolyte, but its hydrophilic character can promote electrolyte spreading and retention under salt-contaminated atmospheric conditions. In contrast, the PDMS-containing surfaces reduce wetting and limit electrolyte/substrate interaction. The best performance is therefore obtained for the SiO_x-CVD+PDMS architecture, where interfacial electrochemical stabilization and hydrophobic wetting control act together.

However, the results discussed so far do not directly prove an adhesion-promoting function of the SiO_x-CVD layer for PDMS grafting. They clearly show that the additional SiO_x-CVD interlayer improves the electrochemical and atmospheric corrosion performance of the final SiO_x-CVD+PDMS architecture. Moreover, the model-substrate experiments discussed in Section 4.1.5 suggest that PDMS-derived interphases are more stable on Si–O(H)-terminated surfaces than on Al–O(H) interfaces. Nevertheless, the direct PDMS modification on polished and etched AlSi10Mg also performs well in the electrochemical and atmospheric corrosion tests. Therefore, the available results do not allow the conclusion that the SiO_x-CVD layer is strictly required for PDMS attachment.

To address this question at least qualitatively, the directly PDMS-modified surface and the SiO_x-CVD+PDMS surface were additionally exposed to ethanolic ODPa solution for 24 h. This experiment was used as a chemical probe to evaluate the accessibility of residual oxide sites and/or the susceptibility of the PDMS-derived interphase to subsequent molecular adsorption. The quantitative XPS results obtained from XPS survey spectra, summarized in Table S5, show a distinctly lower phosphorus signal for the SiO_x-CVD+PDMS surface compared with the directly PDMS-modified surface. The P2s contribution is reduced by approximately 50 %, indicating that less ODPa is adsorbed on the combined modification.

This result suggests that the SiO_x-CVD+PDMS architecture provides fewer ODPa-accessible adsorption sites or a more effectively shielding PDMS-derived interphase. However, this observation should again be interpreted as an indication rather than as direct proof of improved PDMS adhesion. The lower ODPa uptake may result from a denser or more stable PDMS layer on the SiO_x-CVD interlayer, but it may also reflect differences in surface accessibility, oxide chemistry, or the extent of residual unoccupied adsorption sites. Thus, the ODPa post-adsorption experiment supports the assumption that the SiO_x-CVD layer contributes to a more resistant PDMS-based interphase, but it does not unambiguously resolve the exact bonding mechanism.

Consequently, the SiO_x-CVD interlayer is best interpreted not as a strictly necessary prerequisite for PDMS grafting on polished and etched AlSi10Mg, but as a beneficial interfacial layer that improves the functional robustness and reduces the chemical accessibility of the resulting PDMS-based thin-film architecture.

4.3. Combined molecular functionalization of AW2024 by ODPA and ODT

The preceding Sections 4.1 and 4.2 indicated that the formation and stability of molecular and polymer-derived thin-film interphases are strongly influenced by the interfacial chemistry of the substrate surface. While these studies focused on additively manufactured AlSi10Mg and the interaction of PDMS- and ODPA-based modifications with Al- and Si-containing surface domains, the following section transfers this concept to a conventionally processed Al-Cu alloy. In this context, the AW2024-T3 alloy is investigated with respect to the adsorption of self-assembled monolayer-forming molecules bearing different head-group chemistries. The material-specific fundamentals of AW2024, including its heterogeneous intermetallic phase distribution and its associated corrosion behavior, were outlined in Section 2.2.2.

4.3.1. Scope and research question

As an initial observation motivating the present molecular functionalization strategy, unmodified and ODPA-modified AW2024 surfaces were subjected to preliminary atmospheric corrosion exposure using the short-term exposure cell described in Section 3.4.2. Representative images from these preliminary atmospheric corrosion experiments are shown in Figure 48. Under the applied exposure conditions, localized corrosion features were observed at previously identified IMP-containing positions on both the unmodified and the ODPA-modified AW2024 surfaces. Although these experiments were not designed for a quantitative evaluation of atmospheric corrosion performance, they did not reveal a clearly discernible protective effect of the ODPA-only modification with respect to IMP-associated localized corrosion.

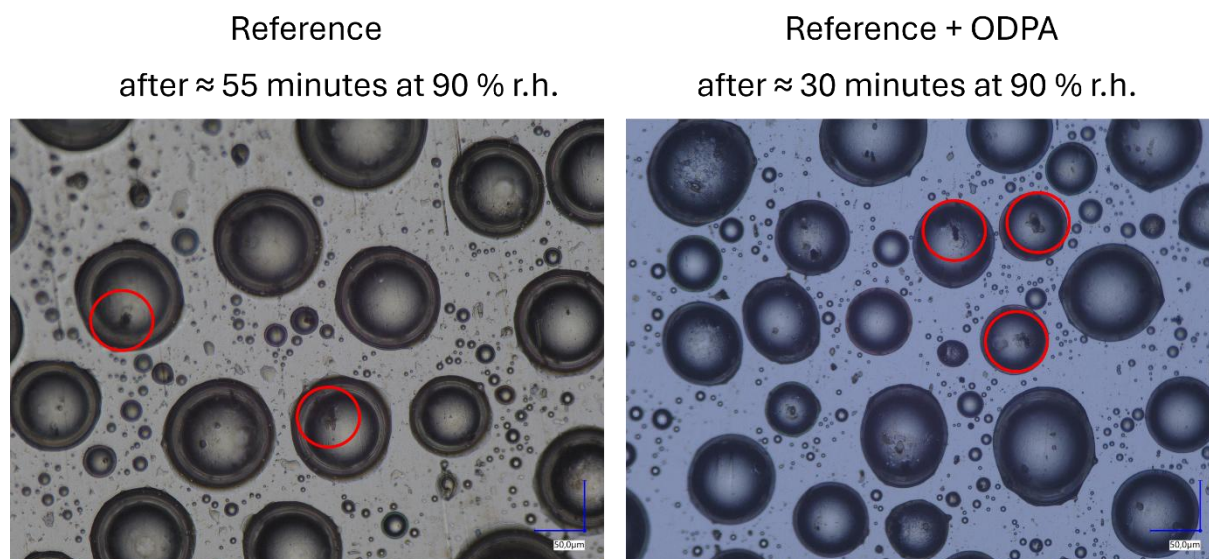


Figure 48. Representative digital microscopy images of NaCl-loaded AW2024 surfaces acquired during preliminary simulated atmospheric corrosion exposure. The exposure was performed in the short-term atmospheric corrosion cell described in Section 3.4.2 at a relative humidity of approximately 90 %r.h. Prior to exposure, the surfaces were spray-coated with NaCl to obtain a surface loading of approximately $100 \mu\text{g} \cdot \text{cm}^{-2}$. The dark circular features correspond to electrolyte droplets formed upon deliquescence of the deposited NaCl. The left image shows unmodified AW2024 surface (Reference) after approximately 55 minutes of exposure. The right image shows ODPa-modified AW2024 surface (Reference+ODPa) after approximately 30 minutes of exposure. Red circles indicate localized corrosion features at positions previously identified as IMP-containing regions by digital microscopy prior to NaCl deposition. Scale bars: 50 μm .

This observation is consistent with the results reported by Kozlica et al., who investigated the inhibition of localized corrosion on AA2024-T3 using octylphosphonic acid under chloride-containing immersion conditions.¹⁹⁶ In their study, the phosphonic-acid-based treatment did not sufficiently suppress localized corrosion activity on the heterogeneous alloy surface. Although their work employed a shorter-chain phosphonic acid and immersion rather than atmospheric exposure conditions, it provides relevant supporting evidence that a phosphonic-acid-based single-component modification may be insufficient to protect all electrochemically active surface domains of AW2024.

One possible explanation for this limited protection is that phosphonic acids preferentially interact with hydroxylated aluminum oxide-rich regions but do not form an equally compact, stable, or well-organized molecular interphase on Cu-containing intermetallic particles of AW2024. As described in Section 2.2.2, this alloy contains chemically and electrochemically distinct intermetallic phases, including Cu-rich particles that can act as local cathodes or become cathodically activated during corrosion. Therefore, a surface modification strategy relying exclusively on the affinity of phosphonic acid groups toward oxidized aluminum-rich regions may leave Cu-rich reaction sites insufficiently protected.

A complementary molecular strategy therefore requires an adsorbate capable of interacting with Cu-rich surface regions. As outlined in Section 2.3.1, thiol-containing molecules are well established for the formation of highly organized molecular layers on copper surfaces due to the pronounced affinity of sulfur toward copper. In addition to their favorable adsorption behavior, alkanethiol-derived molecular layers have been reported to protect copper under accelerated atmospheric corrosion conditions. Hosseinpour et al. investigated self-assembled monolayers of

n-alkanethiols with different chain lengths on copper exposed to humidified air containing formic acid.⁸³ The protective effect increased with increasing alkyl-chain length, with ODT providing the strongest inhibition among the investigated molecules. This behavior was related to the ability of the densely packed long-chain molecular film to retard the transport of corrosion-relevant species toward the copper/SAM interface.

The relevance of substrate chemistry for ODT-based protection was further demonstrated in comparative atmospheric corrosion studies on copper, zinc, and Cu–Zn alloys.¹⁹⁷ In these experiments, ODT protected pure copper substantially more effectively than pure zinc, consistent with the stronger interaction of sulfur with copper. Moreover, ODT provided effective protection on single-phase Cu₂₀Zn brass, whereas its protective performance was distinctly reduced on heterogeneous two-phase Cu₄₀Zn brass.¹⁹⁷ This observation is of particular importance for the present study, since it shows that the favorable behavior of ODT on pure copper or comparatively homogeneous Cu-containing substrates cannot be transferred uncritically to chemically heterogeneous multiphase alloy surfaces.

Based on these findings, ODT was selected as a complementary adsorbate to ODPA. Within the conceptual approach of this section, ODPA is intended to address aluminum oxide-rich surface regions, whereas ODT is intended to interact preferentially with accessible Cu-rich sites. The fundamental feasibility of such a complementary adsorption concept has previously been demonstrated by Schnieders et al. on idealized patterned Al–Cu model substrates.¹⁹⁸ In their study, molecular layers were deposited from a mixed solution containing molecules with phosphonic acid and thiol head groups. Imaging ToF-SIMS analysis revealed a lateral chemical contrast corresponding to the underlying metallic pattern: ODPA-derived species were preferentially detected on the aluminum regions, whereas ODT-derived species were preferentially detected on the copper regions. In combination with PM-IRRAS and water contact angle analysis, these results demonstrated that complementary head-group chemistries can self-localize on spatially separated Al and Cu surface domains and form an alkyl-terminated molecular interphase across an idealized heterogeneous model surface.¹⁹⁸

However, the transfer of this complementary adsorption concept from patterned metallic model substrates to AW2024 is not straightforward. The substrates investigated by Schnieders et al. consisted of comparatively well-defined aluminum and copper regions. In contrast, AW2024 contains Cu-rich intermetallic particles (as well as Fe- and Mn-based IMPs) embedded within an aluminum matrix, and these phases are covered by native oxide structures of complex and spatially varying composition. As discussed in Sections 2.1.2, 2.1.3, and 2.2.2, the oxide chemistry of Al–Cu alloy surfaces depends strongly on the underlying microstructure and may differ between the aluminum matrix and Cu-rich intermetallic regions. Studies on model Al–Cu alloy surfaces suggest that Cu-rich intermetallic phases may be covered by aluminum- and copper-oxide-containing surface structures, while metallic copper can be enriched at or beneath the oxide/metal interface (see Figure 3).⁵⁸ Consequently, the presence of Cu-rich intermetallic particles in AW2024 does not necessarily imply that copper-containing adsorption sites are directly accessible for ODT.

This complex oxide structure is central to the combined ODPA+ODT adsorption strategy investigated in this section. If Cu-rich intermetallic regions are at least partially masked by aluminum oxide-rich surface species, ODT adsorption alone may not efficiently address these sites. In contrast, treatment with a phosphonic acid may influence the aluminum oxide-containing fraction of the surface through adsorption-coupled oxide restructuring or partial oxide dissolution. Hauffman et al. investigated the adsorption of n-octylphosphonic acid on aluminum

oxide from ethanolic solution and reported that molecular deposition was associated with an inhomogeneous organic overlayer and indications of attack on the underlying oxide.¹⁹⁹ This observation is particularly relevant for the present work because the ODPA and ODT treatments are likewise performed from ethanolic solution. It therefore supports the plausibility that an ODPA-containing treatment could modify aluminum oxide-rich regions of the heterogeneous AW2024 surface and potentially alter the accessibility of Cu-rich sites for ODT adsorption.

Nevertheless, this mechanistic interpretation must be regarded as a working hypothesis rather than as an established adsorption pathway for the present system. The observation of oxide modification during alkylphosphonic acid adsorption on homogeneous aluminum oxide does not directly prove that ODPA exposes Cu-containing sites on AW2024 or that ODT subsequently adsorbs selectively on these regions. Furthermore, the native oxide structure of Cu-rich intermetallic particles is considerably more complex than that of a homogeneous aluminum oxide model surface. Thus, the interaction between ODPA, ODT, and the oxide-covered intermetallic microstructure must be evaluated experimentally.

Based on these considerations, the central hypothesis of this section is that a combined ODPA+ODT adsorption strategy may address chemically distinct domains of the heterogeneous AW2024-T3 surface more effectively than an ODPA- or ODT-only modification. In this concept, ODPA is expected to interact preferentially with aluminum oxide-rich regions and may additionally modify Al-oxide-containing contributions above or adjacent to intermetallic particles. ODT is intended to interact with accessible Cu-rich sites and thereby reduce the electrochemical activity of surface regions that remain insufficiently protected by ODPA alone. If successful, such complementary adsorption could reduce local discontinuities within the molecular interphase and influence the corrosion-related electrochemical response of the alloy.

To assess this hypothesis, individual ODPA and ODT modifications as well as combined ODPA+ODT adsorption strategies are investigated. Since the complex phase distribution of AW2024 limits the unambiguous spectroscopic evaluation of phase-selective adsorption, a binary Al–Cu model alloy containing enlarged Al_2Cu regions is additionally employed. This model system is intended to facilitate the spatially resolved investigation of adsorption preferences on Cu-rich phases, whereas electrochemical measurements on AW2024 are used to evaluate the influence of the molecular modification strategy on the interfacial response of the technically relevant alloy.

The investigations presented in this section should be understood as an exploratory evaluation of a complementary molecular functionalization concept. In contrast to the preceding studies, this part of the dissertation is not based on a finalized publication, and the available dataset does not yet provide a complete mechanistic description of selective adsorption on oxide-covered Al–Cu intermetallic phases. Nevertheless, the obtained results provide relevant indications regarding the feasibility and limitations of chemically selective molecular functionalization strategies for heterogeneous AW2024 surfaces and establish a basis for future investigations.

4.3.2. Phase-resolved adsorption studies on the AlCu5.9 model alloy

To facilitate the interpretation of the spatially resolved analysis of ODT-, ODPA-, and combined ODPA+ODT-modified surfaces, a binary AlCu5.9 model alloy was prepared as described in Section 3.1. In contrast to AW2024, which contains several chemically and electrochemically distinct intermetallic phases, as discussed in Section 2.2.2, the model alloy was designed to

represent a simplified Al–Cu system dominated by Al_2Cu regions embedded in an aluminum matrix. This reduced microstructural complexity avoids the need to differentiate between multiple types of intermetallic phases when assigning modification-related signals. Furthermore, the enlarged Al_2Cu regions are expected to facilitate the spatial correlation of adsorption-related signals with the underlying Cu-rich phase during ToF-SIMS analysis.

Before evaluating the molecularly modified surfaces, the microstructure and local elemental composition of the prepared AlCu5.9 model alloy were characterized by SEM and EDS. The corresponding results are presented in Figure 49 and the element quantification obtained from EDS point spectra are summarized in Table 16.

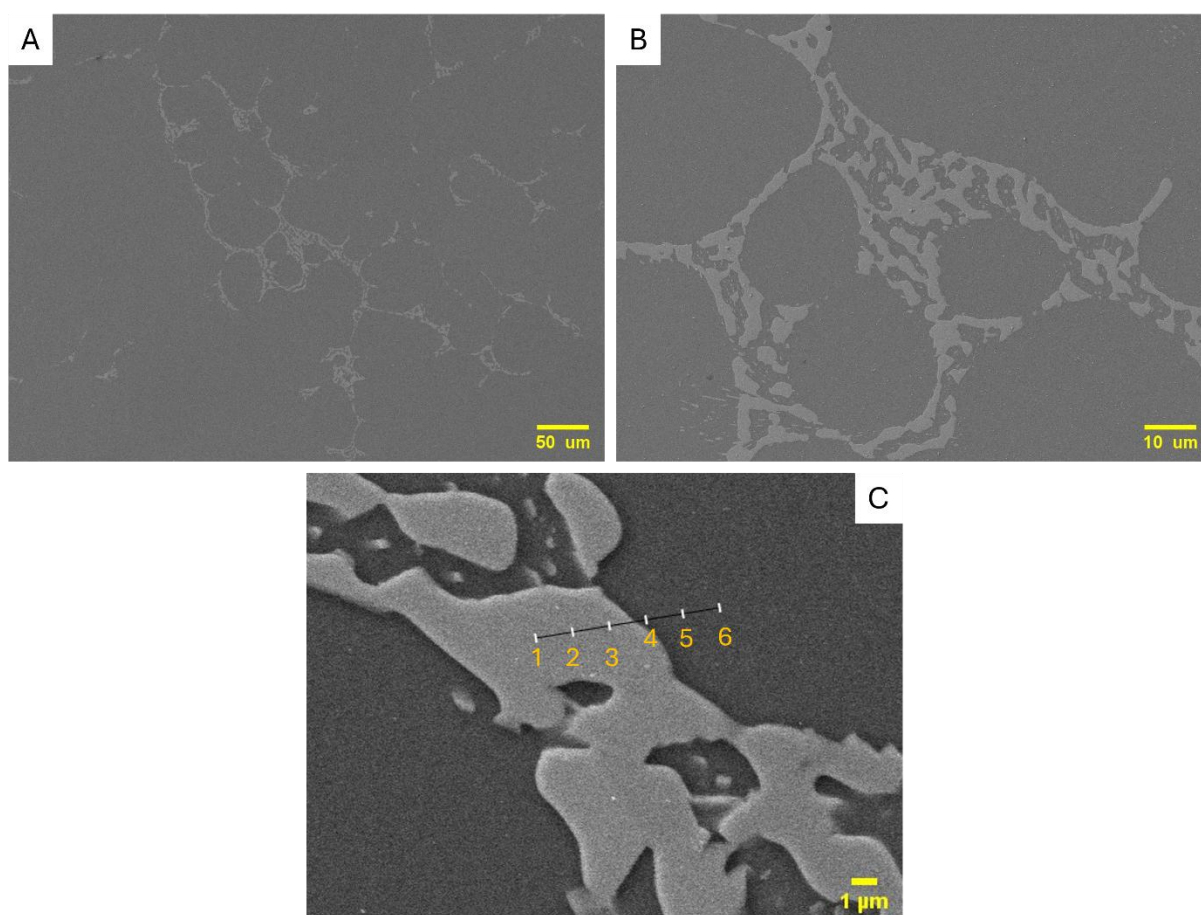


Figure 49. SEM images of the AlCu5.9 model alloy at progressively increasing magnifications. A SE2 detector and an electron acceleration voltage of 2 kV was used for all images. Images (A–C) show the same representative microstructural region, revealing bright interconnected features embedded in a darker matrix. The observed brightness contrast reflects local compositional differences within the alloy. To support phase identification, a series of six EDS point spectra was recorded along a line crossing the bright feature and the surrounding matrix. The positions and numbering of the individual point analyses are indicated in (C). The corresponding elemental compositions are summarized in Table 16.

Figure 49 reveals bright, interconnected microstructural features embedded in a darker matrix. The EDS quantification listed in Table 16 indicates an Al/Cu atomic ratio of approximately 1.6:1 to 1.7:1 for the bright intermetallic features. Although this composition deviates from the ideal stoichiometric ratio of 2:1 expected for Al_2Cu and therefore does not provide an unequivocal phase identification by EDS alone, the results clearly demonstrate a pronounced Cu enrichment

relative to the surrounding Al-rich matrix. Considering the binary Al–Cu composition of the model alloy and its intended use for comparison with Al₂Cu-containing regions of AW2024, the bright intermetallic features are hereafter referred to as Al₂Cu regions for clarity and simplicity. This designation should be understood as an operational assignment for the following adsorption analysis rather than as definitive confirmation of an exactly stoichiometric Al₂Cu phase. These regions nevertheless provide suitable Cu-containing model domains for evaluating spatial adsorption tendencies by ToF-SIMS.

Table 16. Elemental compositions derived from EDS point spectra recorded on the AlCu5.9 model alloy. Values are reported in at.% for the analysis positions 1–6 indicated in Figure 49C $\pm$ the error counts.

Core level	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6
Al K	59.2 $\pm$ 0.3	58.92 $\pm$ 0.3	58.42 $\pm$ 0.3	92.62 $\pm$ 0.4	94.42 $\pm$ 0.4	94.42 $\pm$ 0.4
C K	2.22 $\pm$ 0.2	2.42 $\pm$ 0.2	1.32 $\pm$ 0.1	1.02 $\pm$ 0.1	1.02 $\pm$ 0.1	1.12 $\pm$ 0.1
O K	1.22 $\pm$ 0.2	1.32 $\pm$ 0.1	1.72 $\pm$ 0.2	1.62 $\pm$ 0.2	0.92 $\pm$ 0.1	1.22 $\pm$ 0.2
Cu L	36.82 $\pm$ 0.2	36.62 $\pm$ 0.2	34.62 $\pm$ 0.2	4.42 $\pm$ 0.1	3.32 $\pm$ 0.0	3.22 $\pm$ 0.1
Fe L	0.72 $\pm$ 0.2	0.82 $\pm$ 0.2	4.02 $\pm$ 0.2	0.42 $\pm$ 0.1	0.32 $\pm$ 0.1	0.12 $\pm$ 0.1

Following the microstructural characterization, AlCu5.9 specimens were prepared for ToF-SIMS analysis as described in Sections 3.1, 3.3.1 and 3.3.5,. Four specimens were investigated, each representing one of the surface states considered in this study, i.e. Reference, ODPA, ODT, and ODPA+ODT.

During ToF-SIMS analysis, secondary ion signals were recorded after successive sputter intervals, thereby providing depth-resolved chemical information on the investigated surfaces. In the present study, this approach served two distinct purposes. First, surface-near secondary ion signals characteristic of the molecular modifications were used to assess the lateral distribution of ODPA- and ODT-derived species. Second, secondary ion signals obtained after removal of the organic surface layer and (partial) removal of the native oxide were used to identify the underlying microstructural domains of the AlCu5.9 alloy.

In the initial surface-near depth range, a direct distinction between the Al-rich matrix and the Cu-containing intermetallic regions is impeded by the presence of adventitious adsorbates, the applied molecular modifications, and an Al-dominated oxide layer covering the underlying alloy microstructure. These findings, in principle, align with the proposed model of Cornette et al., which is schematically illustrated in Figure 3.⁵⁸ With increasing sputter time, the contribution of the underlying alloy becomes more pronounced. In particular, the increased Cu-related secondary ion intensity enables the localization of the Cu-containing intermetallic regions, hereafter referred to as Al₂Cu regions, relative to the surrounding Al-rich matrix.

For this purpose, phase-identifying secondary ion intensity (SII) maps were generated by averaging specimen-specific z-depth ranges of interest (ZROIs), within which the underlying alloy microstructure becomes distinguishable. The individual ZROIs used for each surface state are specified in the captions of Figure 50 and Figure 51. To improve the signal-to-noise ratio of the phase identification, each phase-associated SII map represents the summed intensity of several characteristic secondary ion fragments. The combinations of secondary ion fragments used to represent the individual microstructural domains are specified in Section 3.5.6. Based on the resulting Al/Cu-related contrast, regions of interest (ROIs) corresponding to the Al-rich matrix and the operationally defined Al₂Cu regions were assigned, as indicated in Figure 50 and Figure 51. These phase-specific ROIs were subsequently transferred to the surface-near secondary ion data containing ODPA- and ODT-related fragment signals. In this way, the lateral distribution of the molecular species could be correlated with the underlying microstructural domains in order to evaluate possible preferential adsorption tendencies of ODPA and ODT.

The SII maps shown in Figure 50 and Figure 51 support the SEM/EDS-based phase assignment, as the regions operationally referred to as Al₂Cu regions exhibit increased Cu-related secondary ion intensities compared with the surrounding Al-rich matrix.

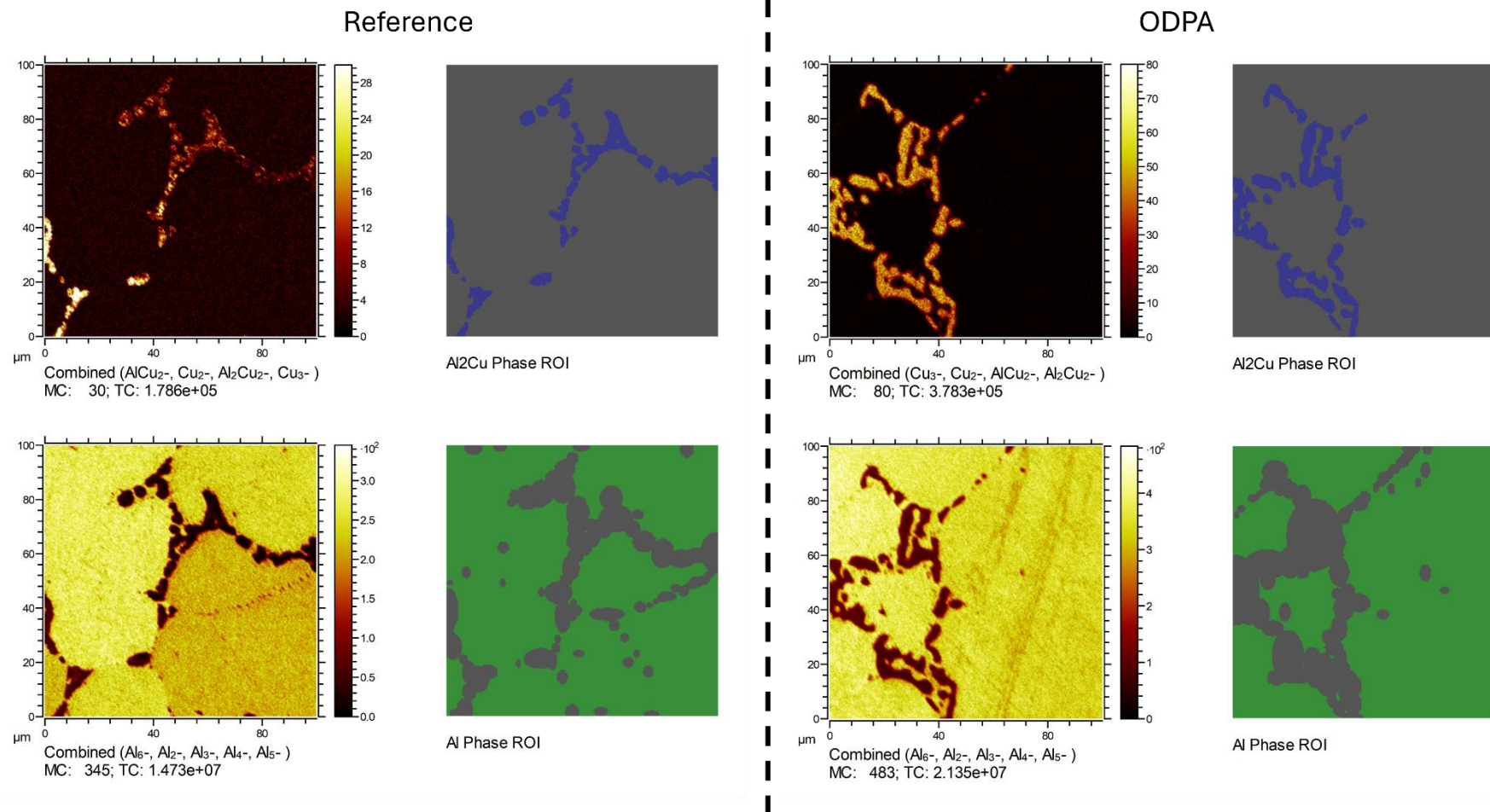


Figure 50. ToF-SIMS secondary ion intensity (SII) maps used for phase-specific ROI definition on the Reference and ODP-modified AlCu5.9 model-alloy surfaces. The left and right columns correspond to the Reference and ODP surface states, respectively. The SII maps were generated from selected depth ranges of interest (ZROIs), within which the underlying alloy microstructure becomes distinguishable. The evaluated ZROIs correspond to sputter-time intervals of 162-793 s for the Reference surface and 148-1218 s for the ODP-modified surface. The upper panels show combined secondary ion signals associated with the Cu-containing intermetallic regions, operationally referred to as Al₂Cu regions, whereas the lower panels show signals associated with the surrounding Al-rich matrix. Based on this phase-related contrast, regions of interest (ROIs) were defined for the subsequent evaluation of surface-near, modification-related secondary ion fragments. Blue areas indicate Al₂Cu-region ROIs, green areas indicate Al-matrix ROIs, and grey areas represent regions excluded from further analysis.

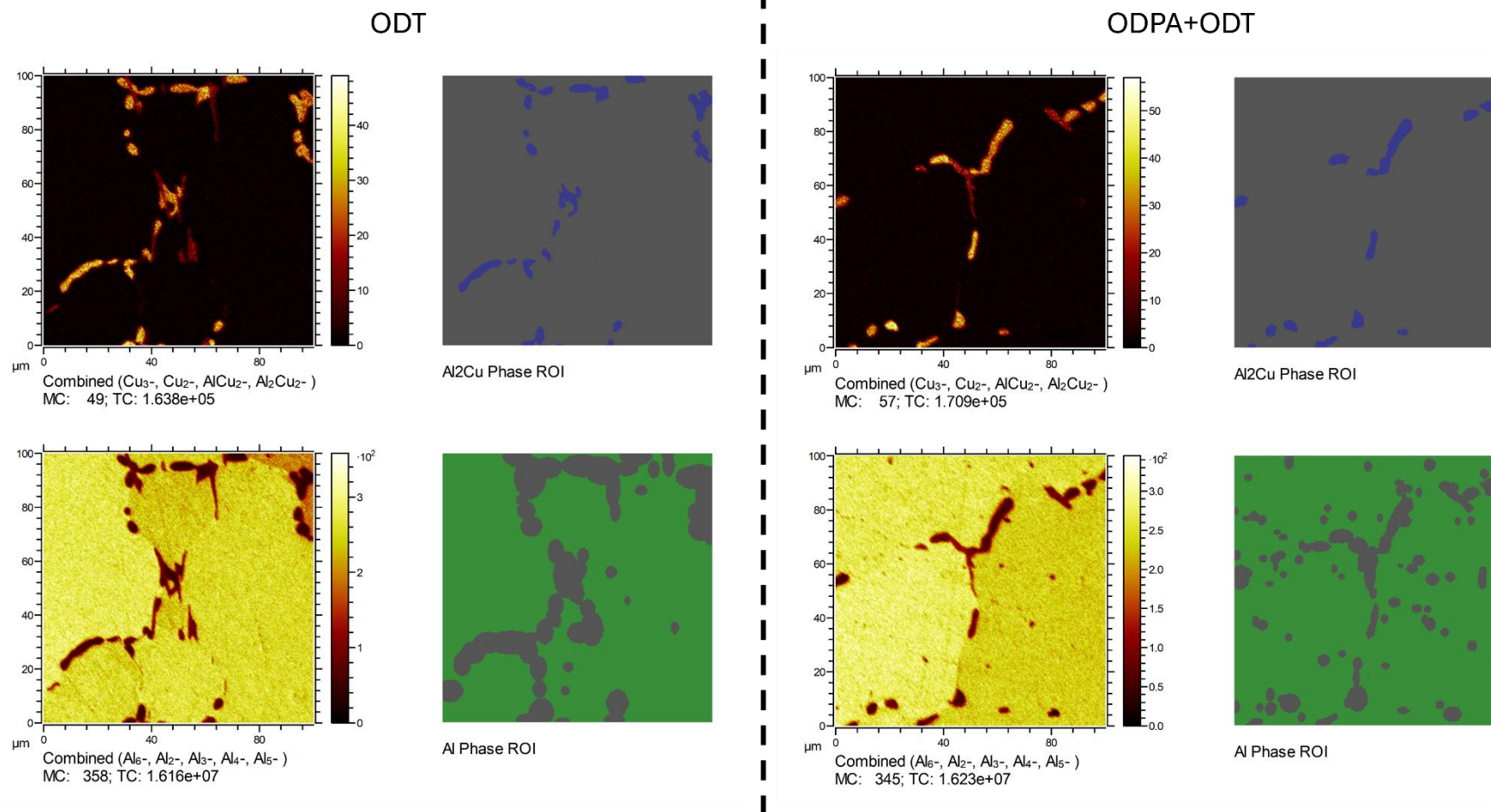


Figure 51. ToF-SIMS secondary ion intensity (SII) maps used for phase-specific ROI definition on the ODT- and ODTA+ODT-modified AlCu5.9 model-alloy surfaces. The left and right columns correspond to the ODT and ODTA+ODT surface states, respectively. The SII maps were generated from selected depth ranges of interest (ZROIs), within which the underlying alloy microstructure becomes distinguishable. The evaluated ZROIs correspond to sputter-time intervals of 136-933 s for the ODT-modified surface and 152-805 s for the ODTA+ODT-modified surface. The upper panels show combined secondary ion signals associated with the Cu-containing intermetallic regions, operationally referred to as Al_2Cu regions, whereas the lower panels show signals associated with the surrounding Al-rich matrix. Based on this phase-related contrast, regions of interest (ROIs) were defined for the subsequent evaluation of surface-near, modification-related secondary ion fragments. Blue areas indicate Al_2Cu -region ROIs, green areas indicate Al-matrix ROIs, and grey areas represent regions excluded from further analysis.

Based on the phase-specific ROIs defined in Figure 50 and Figure 51, the surface-near secondary ion signals were subsequently evaluated with respect to the molecular modifications. P^- -ions were used as indicators for ODPA-derived species, whereas S^- -ion fragments were used as indicators for ODT-derived species. For each surface state, the P^- and S^- intensities represent the summed signals of the respective selected fragments integrated over the initial sputter interval from 0 to 25 s. Based on the approximated sputter rate (see Section 3.5.6), this interval corresponds to a depth of about 2 nm. This interval was selected based on the complete sputter profiles provided in Figure S10, which indicate the presence of modification-related surface species within this initial measurement range. The corresponding signal intensities within the predefined Al-matrix and Al_2Cu -region ROIs were compared in order to evaluate possible phase-correlated localization tendencies of the adsorbed molecules.

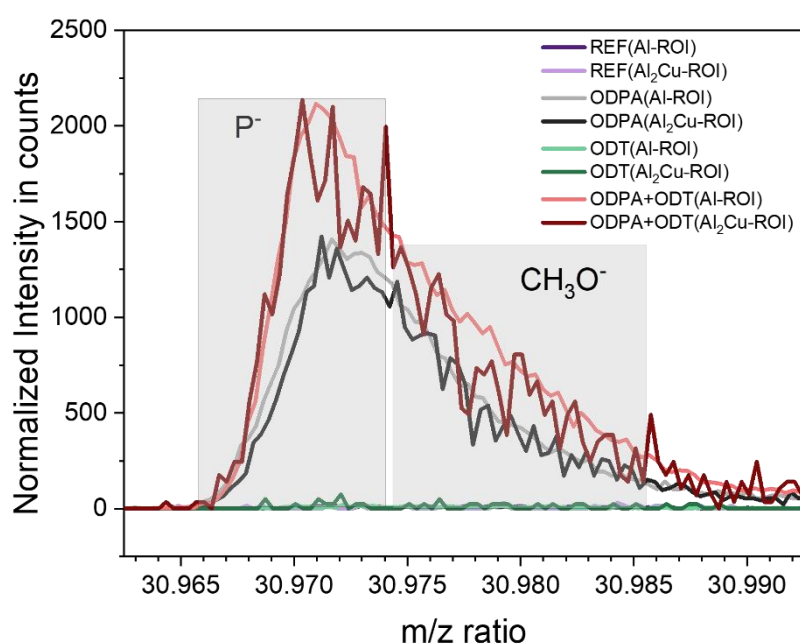


Figure 52. Surface-near P^- -related ToF-SI mass spectra of the investigated $AlCu_{5.9}$ model-alloy surface states. The spectra were evaluated within the predefined Al-rich matrix and Al_2Cu -region ROIs derived from the phase-specific SII maps shown in Figure 50 and Figure 51. For each ROI, the SII were summed over the initial sputter interval from 0 to 25 s. Spectra are shown for the Reference, ODPA-, ODT-, and ODPA+ODT-modified surfaces, with the corresponding ROI assignments indicated in the legend. The highlighted mass ranges correspond to the P^- -signal used as an indicator for ODPA-derived species and the adjacent CH_3O^- -contribution. The indicated P^- -mass interval was used to calculate the corresponding P^- -related secondary ion intensities in the sputter profiles (see Figure S10) and for the subsequent ROI-based evaluation.

The P^- -intensities obtained within the predefined ROIs are shown in Figure 52. For the Reference and ODT-modified surface states, only negligible P^- -signal intensities are detected in both the Al-rich matrix and the Al_2Cu regions. This confirms that the evaluated P^- -ions are suitable indicators for ODPA-derived species under the applied measurement conditions.

In contrast, both surface states treated with ODPA-containing solutions exhibit strongly increased P^- -intensities in both microstructural regions. Thus, ODPA-derived species are detected not only on the Al-rich matrix but also within the ROIs assigned to the Cu-containing intermetallic regions.

The ODPA+ODT-modified surface exhibits higher P^- -intensities than the ODPA-only surface in both types of ROIs. This observation suggests that the presence of ODT during the combined treatment influences the resulting ODPA-related surface signal. However, a mechanistic explanation for this increase cannot be derived from the present dataset. In particular, it cannot be concluded whether the increased P^- -intensity originates from enhanced ODPA adsorption, changes in molecular organization or fragmentation behavior, or ToF-SIMS matrix effects.

When comparing the Al-rich matrix and the Al_2Cu -region ROIs within the ODPA-containing surface states, no pronounced phase-related difference in the P^- -intensities is observed. Therefore, the P^- -related data do not indicate a preferential localization of ODPA-derived species on either of the investigated microstructural regions. This finding may be related to the complex oxide-covered nature of the AlCu5.9 surface: oxygen-containing surface species capable of interacting with phosphonic acid groups may be present both on the Al-rich matrix and on the Cu-containing intermetallic regions. Consequently, the presence of Cu-enriched domains does not exclude ODPA-derived species from these regions. This is not surprising, because it is known, that ODPA can also adsorb on Cu/Cu_{ox} surfaces.²⁰⁰

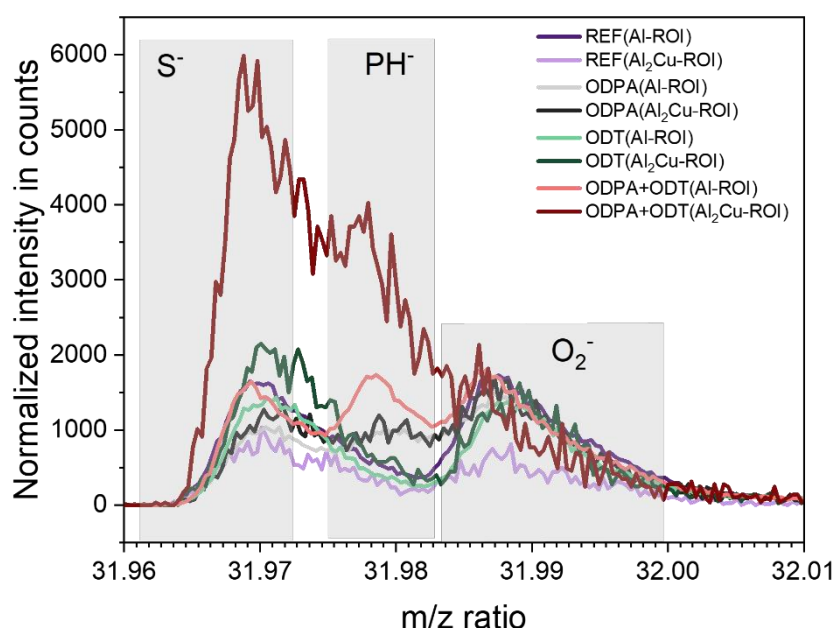


Figure 53. Surface-near S^- -related ToF-SI mass spectra of the investigated AlCu5.9 model-alloy surface states. The spectra were evaluated within the predefined Al-rich matrix and Al_2Cu -region ROIs derived from the phase-specific SII maps shown in Figure 50 and Figure 51. For each ROI, the secondary ion intensities were summed over the initial sputter interval from 0 to 25 s. Spectra are shown for the Reference, ODPA-, ODT-, and ODPA+ODT-modified surfaces, with the corresponding ROI assignments indicated in the legend. The highlighted mass ranges correspond to the S^- -signal used as an indicator for ODT-derived species and the adjacent PH^- - and O_2^- -contribution. The indicated S^- -mass interval was used to calculate the corresponding S^- -related secondary ion intensities in the sputter profiles (see Figure S10) and for the subsequent ROI-based evaluation. Since measurable S^- -signals are also detected for the Reference surface, ODT-related contributions are interpreted based on the signal increase relative to the corresponding control surface states.

The S^- -mass spectra evaluated within the predefined ROIs are shown in Figure 53. Analogous to the P^- -analysis, the secondary ion intensities were summed over the initial sputter interval from

0 to 25 s. In contrast to the P^- -signal, measurable S^- -intensities are already detected for the Reference surface in both the Al-rich matrix and the operationally defined Al_2Cu regions. Thus, the S^- -signal cannot be regarded as an exclusively ODT-specific indicator without consideration of the corresponding control surface states.

Nevertheless, a pronounced increase in the S^- -signal is observed within the Al_2Cu -region ROIs for the surface states treated with ODT-containing solutions, i.e. ODT and ODPA+ODT, compared with the Reference and ODPA-treated surfaces. In contrast, the ODPA-modified surface does not exhibit a clear increase in S^- -intensity within the Al_2Cu -region ROI relative to the Reference. This comparison indicates that the increased S^- -intensities detected for the ODT-containing surface states are associated with the presence of ODT-derived species.

Notably, the ODPA+ODT-modified surface exhibits a higher S^- intensity within the Al_2Cu -region ROI than the ODT-only surface. This observation may indicate that the presence of ODPA during the combined treatment influences the localization or detectability of ODT-derived species on Cu-containing intermetallic regions. One possible explanation is that ODPA-induced modification or restructuring of Al-oxide-containing surface species increases the accessibility of Cu-containing adsorption sites for ODT. However, this interpretation remains hypothetical, since the present data cannot distinguish between enhanced ODT localization, changes in molecular organization, variations in secondary ion yield, or other matrix-related effects.

No comparably clear trend is observed for the S^- -intensities within the Al-rich matrix ROIs, which is in alignment with Ref¹⁹⁸. More importantly, for both ODT-containing surface states, the S^- -signal intensity is distinctly higher in the Al_2Cu -region ROI than in the corresponding Al-rich matrix ROI. Within the limitations of the ToF-SIMS analysis, this phase-correlated signal distribution suggests a preferential localization tendency of ODT-derived species on the Cu-containing intermetallic regions of the AlCu5.9 model alloy. This finding is consistent with the intended complementary adsorption concept, in which ODT preferentially addresses accessible Cu-rich surface sites.

Overall, the ToF-SIMS analysis of the AlCu5.9 model alloy partially supports the complementary molecular functionalization concept developed in Section 4.3.1. While ODPA-derived species are detected on both investigated microstructural regions without a clear localization preference, ODT-derived species show a pronounced signal enrichment on the Cu-containing Al_2Cu regions. The combined ODPA+ODT treatment therefore appears capable of retaining ODPA-derived species across the oxide-covered alloy surface while promoting an increased ODT-related signal contribution at Cu-rich intermetallic regions.

Nevertheless, these results should be interpreted as indications of phase-correlated molecular localization rather than as definitive proof of quantitatively selective adsorption. ToF-SIMS secondary ion intensities are influenced by the local chemical matrix, and the AlCu5.9 model alloy represents a simplified Al-Cu microstructure that does not fully reproduce the phase diversity and oxide complexity of AW2024. The following sections therefore transfer the individual and combined molecular modification strategies to the technically relevant AW2024 alloy. PM-IRRAS and WCA measurements are used to evaluate whether the applied treatments modify the overall surface chemistry and wettability, while electrochemical measurements are used to assess their influence on the corrosion-related interfacial response. Accordingly, the AW2024 investigations address the functional relevance of the molecular modification strategy rather than providing direct evidence for phase-selective adsorption on the engineering alloy surface.

4.3.3. Surface properties of ODPA- and ODT-treated AW2024

A direct phase-resolved evaluation of molecular adsorption on AW2024 is considerably complicated by its heterogeneous distribution of chemically distinct, micrometer- and submicrometer-sized intermetallic particles and by the spatially varying oxide chemistry associated with these phases. An unambiguous correlation of molecule-related signals with individual IMP types would therefore require highly sensitive spatially resolved analyses and remains beyond the scope of the present evaluation. For this reason, phase-correlated adsorption tendencies were investigated on the simplified AlCu5.9 model alloy in Section 4.3.2. The investigations on AW2024 presented in the following instead focus on the overall surface changes and functional interfacial response resulting from the individual and combined ODPA- and ODT-based treatments.

For this purpose, dynamic water contact angle measurements were first used to evaluate whether the molecular treatments alter the macroscopic wettability of the AW2024 surface. PM-IRRAS measurements were then employed to assess whether these wetting changes are accompanied by molecule-related vibrational features associated with alkyl-chain-containing surface species.

To evaluate whether the molecular treatments affect the macroscopic wettability of the AW2024 surface, dynamic water contact angle measurements were performed. In contrast to a single static contact angle value, the advancing contact angle (θ_{adv}) describes the wetting response during expansion of the liquid droplet, whereas the receding contact angle (θ_{rec}) is particularly sensitive to contact-line pinning and local surface heterogeneities. The difference between both values, referred to as contact angle hysteresis (CAH), therefore provides additional information on the uniformity of the resulting outer interface. The advancing and receding water contact angles as well as the corresponding hysteresis values are summarized in Table 17.

Table 17. Dynamic water contact angle measurements of the investigated AW2024 surface states. Mean advancing contact angles (θ_{adv}), receding contact angles (θ_{rec}), and the resulting contact angle hysteresis ($CAH = \theta_{adv} - \theta_{rec}$) are reported with their corresponding standard deviations. For each surface state, two independently prepared samples were analyzed, with two measurements performed on each Reference sample and three measurements performed on each modified sample.

Surface state	θ_{adv} in °	θ_{rec} in °	$\theta_{adv} - \theta_{rec}$ in °
Reference	29.9 ± 7.2	22.5 ± 7.2	7.4 ± 2.7
ODPA	125.9 ± 6.5	114.3 ± 6.5	11.6 ± 2.7
ODT	66.3 ± 4.1	51.4 ± 3.1	14.9 ± 0.8
ODPA+ODT	129.6 ± 1.9	118.3 ± 1.4	11.3 ± 2.3

The untreated Reference surface exhibits low θ_{adv} and θ_{rec} of $29.9 \pm 7.2^\circ$ and $22.5 \pm 7.2^\circ$, respectively, confirming the hydrophilic character of the oxide-covered AW2024 surface. In contrast, treatment with ODPA results in a pronounced increase in θ_{adv} to $125.9 \pm 6.5^\circ$ and in θ_{rec}

to $114.3 \pm 6.5^\circ$. This substantial change in wettability is consistent with the formation of an alkyl-terminated hydrophobic outer interface after ODPA treatment.

The ODT-treated AW2024 surface shows an intermediate wetting response, with an advancing contact angle of $66.3 \pm 4.1^\circ$ and a receding contact angle of $51.4 \pm 3.1^\circ$. Thus, ODT treatment increases the hydrophobicity of the surface compared with the Reference, but does not result in a comparably water-repellent interface as observed after ODPA treatment. This behavior is qualitatively compatible with the ToF-SIMS results obtained on the AlCu5.9 model alloy, where S^- -related signals attributed to ODT-derived surface species showed a pronounced localization tendency within the Cu-containing Al_2Cu regions and no profound adsorption on the Al-matrix. Since Cu-containing intermetallic regions represent only a fraction of the heterogeneous AW2024 surface, preferential interaction of ODT with such domains would not necessarily lead to a uniformly hydrophobic outer interface. However, this comparison should be regarded as a qualitative correlation, since the ToF-SIMS and wettability measurements were performed on different alloy systems and water contact angle measurements do not provide phase-resolved information.

The combined ODPA+ODT treatment yields the highest mean contact angles, with an θ_{adv} of $129.6 \pm 1.9^\circ$ and a θ_{rec} of $118.3 \pm 1.4^\circ$. These values are only slightly higher than those measured for the ODPA-treated surface and remain comparable within the experimental scatter. Consequently, the macroscopic wetting response of the combined treatment appears to be largely governed by the formation of an extended alkyl-terminated hydrophobic outer interface, similar to that obtained after ODPA treatment alone. At the same time, the ToF-SIMS results on the AlCu5.9 model alloy indicate that ODT-derived species may additionally localize preferentially at Cu-containing intermetallic regions during combined treatment. The high water contact angles measured for the ODPA+ODT-treated AW2024 surface are therefore compatible with the complementary molecular functionalization concept, although they do not independently demonstrate phase-selective adsorption.

The contact angle hysteresis further distinguishes the wetting behavior of the investigated surfaces. The Reference surface exhibits a CAH of $7.4 \pm 2.7^\circ$, whereas the ODPA-, ODT-, and ODPA+ODT-treated surfaces show values of $11.6 \pm 2.7^\circ$, $14.9 \pm 0.8^\circ$, and $11.3 \pm 2.3^\circ$, respectively. The highest hysteresis is observed for the ODT-treated surface. This observation is compatible with increased contact-line pinning on a chemically non-uniform outer interface, which may arise if ODT-derived species preferentially interact with specific Cu-containing surface regions rather than forming an extended hydrophobic layer across the complete alloy surface. In contrast, the similar CAH values obtained for the ODPA- and ODPA+ODT-treated surfaces are consistent with a similar chemical and/or structural surface.

Overall, the dynamic contact angle measurements show that ODPA-containing treatments produce strongly hydrophobic AW2024 surfaces, whereas treatment with ODT alone results in only a moderate increase in water repellency. In combination with the ToF-SIMS findings obtained on the AlCu5.9 model alloy, these results are compatible with a functionalization concept in which ODPA-derived species are present on both the Al-rich matrix and the Cu-containing intermetallic regions, whereas ODT-derived species exhibit a preferential localization tendency on the Cu-containing regions. Accordingly, ODPA appears to govern the macroscopic hydrophobicity of the treated AW2024 surfaces, while ODT may contribute complementary functionalization of Cu-containing intermetallic regions. However, since the contact angle measurements provide no phase-resolved information and the ToF-SIMS analysis was performed

on a simplified model alloy, this interpretation should be regarded as supporting evidence rather than as direct proof of phase-selective adsorption on AW2024.

To spectroscopically assess whether the observed changes in wettability are associated with the presence and organization of alkyl-chain-containing surface species, PM-IRRAS measurements were performed on the same set of surface states. Due to pronounced intensity variations between individual PM-IRRAS measurements, the spectra shown in Figure 54 are presented with normalized intensities.

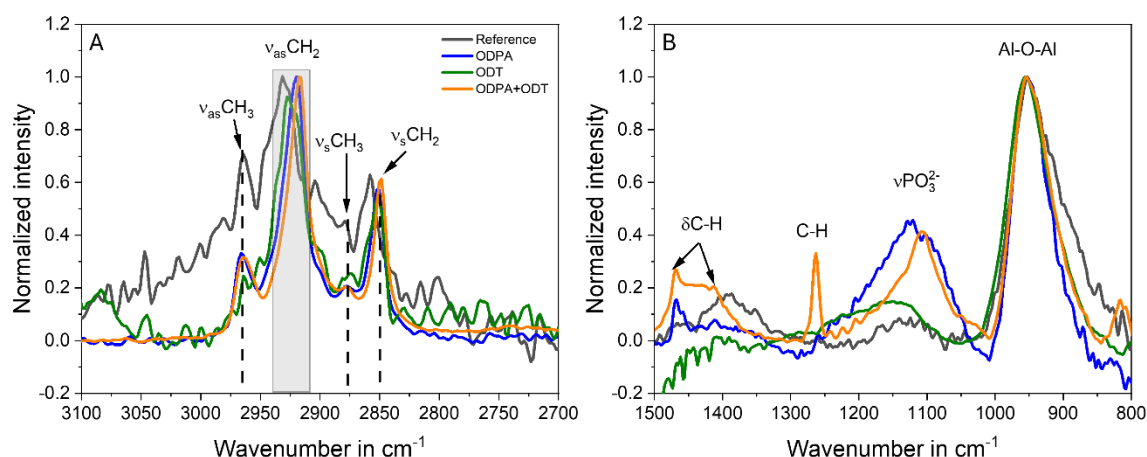


Figure 54. PM-IRRAS spectra of untreated and molecularly treated AW2024 surfaces. Spectra are shown for the Reference, ODPA-, ODT-, and ODPA+ODT-treated surface states. (A) C-H stretching region between 3100 and 2700 cm^{-1} , with characteristic CH_3 and CH_2 stretching band positions indicated. (B) Fingerprint region between 1500 and 800 cm^{-1} , with selected characteristic band positions assigned to the applied molecular treatments. Due to pronounced intensity variations between individual PM-IRRAS measurements, all spectra are presented with normalized intensities.

Figure 54A shows the characteristic C–H stretching region of the investigated AW2024 surface states. C–H stretching bands are observed for all spectra, including the untreated Reference surface. For the Reference, these contributions are attributed to adventitious carbon species and are therefore used as a background reference for distinguishing C–H bands related to the applied molecular treatments. Compared with the Reference, the methylene C–H stretching bands of the treated surfaces appear at lower wavenumbers, as expected for alkyl chains with higher conformational order, in agreement with the previous discussion in Section 4.1.4 and the theoretical background outlined in Section 2.3.1.

The asymmetric methylene stretching bands $\nu_{\text{as}}\text{CH}_2$ are located at 2931, 2920, 2927, and 2917 cm^{-1} for the Reference, ODPA, ODT, and ODPA+ODT surface states, respectively. The corresponding symmetric methylene stretching bands $\nu_{\text{s}}\text{CH}_2$ appear at 2858, 2851, 2851, and 2849 cm^{-1} . Based on these band positions, the apparent conformational order of the alkyl chains follows the trend $\text{ODPA+ODT} > \text{ODPA} > \text{ODT}$.^{82,181,182} However, the conformational order inferred for ODPA+ODT and ODPA is very similar. In contrast, the ODT-treated surface exhibits comparatively higher methylene stretching frequencies, indicating a less ordered alkyl-chain arrangement. This is consistent with the lower macroscopic hydrophobicity observed by WCA and with the ToF-SIMS results on the AlCu5.9 model alloy, which indicated that ODT-derived species preferentially localize on Cu-containing intermetallic regions rather than forming an extended

molecular layer over the complete alloy surface. The slightly lower CH₂ band positions observed for ODPA+ODT compared with ODPA may indicate a marginally improved alkyl-chain organization after combined treatment. This observation is compatible with the assumption that the simultaneous presence of both SAM molecules influences the assembly process, although a mechanistic explanation cannot be derived from the PM-IRRAS data alone.

Figure 54B shows the fingerprint region for all investigated surface states. The dominant band observed for all spectra at approximately 950 cm⁻¹ is assigned to Al–O–Al vibrations originating from the native aluminum oxide. The ODPA-containing surface states exhibit distinct C–H bending vibrations, δ C–H, at 1467 and 1411 cm⁻¹, which are attributed to the alkyl chains of the adsorbed molecules.^{85,177,180} In addition, a broad band appears in the range between 1000 and 1200 cm⁻¹, which can be assigned to PO₃²⁻ stretching vibrations.^{177,201} These spectral features support the presence of ODPA-derived species on the ODPA- and ODPA+ODT-treated AW2024 surfaces.

A band at 1263 cm⁻¹ is observed for the ODPA+ODT-treated surface but is not clearly present for the ODPA-only surface. The origin of this band cannot be unambiguously assigned based on the present data. Based on spectral curves obtained on PDMS-grafted surfaces (see Section 4.1.4 and 4.2.3) and Ref.²⁰², it may be related to C–H vibrations, but this interpretation remains tentative. Moreover, this band is not consistently reported in the literature for ODPA-modified aluminum surfaces. For example, Thissen et al. reported PM-IRRAS spectra of ODPA adsorbed on aluminum in which this band was not observed.¹⁸³ Therefore, the 1263 cm⁻¹ contribution is not used as a primary indicator for ODPA adsorption in the present discussion.

For the ODT-treated surface, the broad spectral contribution around 1200 cm⁻¹ may be related to C–H vibrations, as reported by Alwis et al. for ODT adsorbed on Au surfaces.²⁰² However, this assignment must be treated with caution because the reference system differs substantially from the oxide-covered AW2024 surface investigated here. Since this contribution is the only clearly distinguishable feature in the fingerprint region of the ODT-treated surface, PM-IRRAS alone does not provide a robust verification of ODT adsorption on AW2024. The presence and localization of ODT-derived species are therefore primarily discussed based on the ToF-SIMS results obtained on the AlCu5.9 model alloy and the complementary WCA and electrochemical data.

Overall, the PM-IRRAS results indicate that ODPA-containing treatments generate a more pronounced spectroscopic signature of alkyl-chain-containing molecular species than ODT treatment alone. The CH₂ stretching band positions further suggest that ODPA-derived layers exhibit a higher apparent conformational order than the ODT-treated surface, while the ODPA+ODT treatment shows a slightly improved or at least comparable alkyl-chain order relative to ODPA alone. These findings are consistent with the WCA results, where ODPA and ODPA+ODT produce strongly hydrophobic AW2024 surfaces, whereas ODT alone leads only to a moderate increase in water repellency.

4.3.4. Electrochemical analysis of ODPA- and ODT-monolayer covered AW2024

After evaluating the influence of the molecular treatments on the macroscopic wettability and spectroscopic surface characteristics of AW2024, their functional effect on the electrochemical interfacial response was investigated using EIS and LSV measurements. As outlined above, the electrochemical measurements were performed in a chloride-free, deliberately less aggressive electrolyte in order to minimize rapid chloride-induced localized corrosion and the associated

alteration of the initially established molecular interphase. Accordingly, the measurements are intended to assess functional differences between the molecular treatment strategies under conditions that reduce corrosion-induced alteration of the treated surfaces.

The electrochemical response of the investigated AW2024 surface states was evaluated by EIS and LSV measurements in chloride-free 0.1 M Na₂SO₄ electrolyte. The EIS spectra were fitted using the same modified Randles-type equivalent circuit as applied in Section 4.2.5, allowing changes in charge-transfer resistance and non-ideal capacitive behavior to be compared. Again, the C_{eff} has been calculated according to eq. (2-46). The LSV curves were evaluated by Tafel analysis according to the approach described in Section 2.4.3.2. Representative EIS and LSV data are shown in Figure 55.

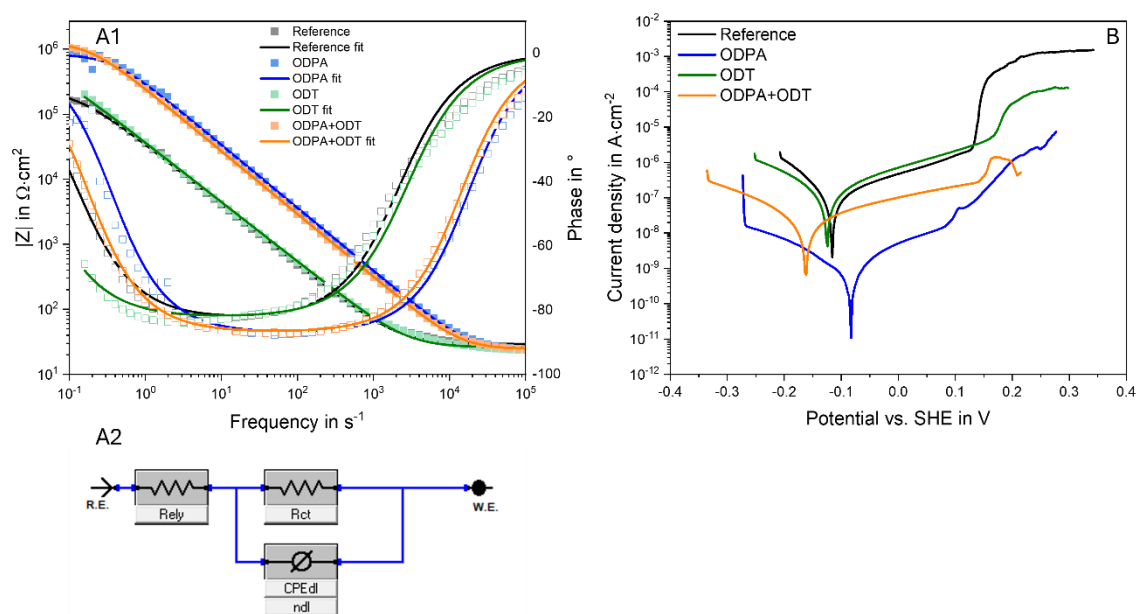


Figure 55. Representative EIS and LSV results of untreated and molecularly treated AW2024 surfaces measured in chloride-free 0.1 M Na₂SO₄ electrolyte. The investigated surface states are the unmodified Reference surface and the ODPa-, ODT-, and ODPa+ODT-treated surfaces. (A1) Representative EIS spectra with the corresponding fits obtained using the equivalent circuit shown in (A2). (A2) Equivalent circuit employed for fitting the impedance spectra, consisting of the electrolyte resistance (R_{ely}) in series with a parallel combination of the charge-transfer resistance (R_{ct}) and the constant phase element (CPE_{dl}) accounting for the double-layer capacitance. (B) Representative LSV curves recorded following EIS characterization of the respective surfaces.

The EIS fit parameters summarized in Table 18 reveal distinct effects of the individual molecular treatments on the electrochemical interfacial response of AW2024 in chloride-free 0.1 M Na₂SO₄ electrolyte.

Table 18. Equivalent-circuit fitting results for the electrochemical characterization of the investigated AW2024 surface states. The parameters were obtained from fits of the EIS spectra shown in Figure 55A1 with the equivalent circuit model shown in Figure 55A2.

Surface state	$R_{ely}/$ $\Omega \cdot \text{cm}^2$	$R_{ct}/$ $\text{M}\Omega \cdot \text{cm}^2$	$Q_{CPE,dl}/$ $\mu\text{F} \cdot \text{cm}^{-2} \cdot \text{s}^{n-1}$	n_{dl}	$\chi^2 \cdot 10^{-3}$	$C_{eff}/$ $\mu\text{F} \cdot \text{cm}^{-2}$
Reference	34.9 ± 13.5	0.30 ± 0.21	5.18 ± 0.28	0.92 ± 0.01	7.3 ± 3.1	3.11 ± 0.18
ODPA	69.9 ± 64.5	0.58 ± 0.20	0.64 ± 0.08	0.97 ± 0.01	6.6 ± 2.2	0.54 ± 0.04
ODT	27.4 ± 13.8	0.73 ± 0.49	5.11 ± 0.35	0.92 ± 0.01	7.4 ± 2.3	3.0 ± 0.53
ODPA+ODT	25.8 ± 12.2	1.94 ± 1.42	0.71 ± 0.14	0.97 ± 0.01	1.2 ± 0.3	0.52 ± 0.08

Relevant differences are observed for the charge-transfer resistance R_{ct} . The untreated Reference surface exhibits the lowest R_{ct} value of $0.30 \pm 0.21 \text{ M}\Omega \cdot \text{cm}^2$, indicating the highest interfacial electrochemical activity among the investigated surface states. All molecularly treated surfaces show increased R_{ct} values. ODPA treatment increases R_{ct} to $0.58 \pm 0.20 \text{ M}\Omega \cdot \text{cm}^2$, while ODT treatment results in a slightly higher value of $0.73 \pm 0.49 \text{ M}\Omega \cdot \text{cm}^2$. The combined ODPA+ODT treatment yields the highest charge-transfer resistance of $1.94 \pm 1.42 \text{ M}\Omega \cdot \text{cm}^2$. Although the standard deviation is large, it should be noted that the ODPA+ODT dataset comprises the highest number of individual measurements ($n = 10$), providing a comparatively robust basis for evaluating this trend. The results suggest that the combined molecular treatment most effectively reduces interfacial charge-transfer processes under the applied chloride-free conditions.

The capacitive response further differentiates the influence of the individual molecules. The Reference surface exhibits an effective capacitance (C_{eff}) of $3.11 \pm 0.18 \mu\text{F} \cdot \text{cm}^{-2}$. A comparable value is obtained for the ODT-treated surface, with $C_{eff} = 3.00 \pm 0.53 \mu\text{F} \cdot \text{cm}^{-2}$, indicating that ODT alone does not substantially alter the global capacitive behavior of the AW2024/electrolyte interface. In contrast, ODPA-containing treatments strongly reduce the effective capacitance to $0.54 \pm 0.04 \mu\text{F} \cdot \text{cm}^{-2}$ for ODPA and $0.52 \pm 0.08 \mu\text{F} \cdot \text{cm}^{-2}$ for ODPA+ODT. This decrease is consistent with the formation of an extended hydrophobic molecular interphase, which increases the effective dielectric thickness and/or reduces the electrochemically accessible surface area.

The CPE exponent (n_{dl}) supports this interpretation. While the Reference and ODT-treated surfaces show values of 0.92, the ODPA and ODPA+ODT surfaces exhibit slightly higher values of 0.97. This indicates a more ideal capacitive response after ODPA-containing treatments, which is consistent with a more coherent outer molecular interface. In contrast, the ODT-treated surface behaves more similarly to the Reference with respect to its capacitive response, in agreement with the dynamic contact angle results and the ToF-SIMS analysis on the AlCu5.9 model alloy, which suggested a more localized interaction of ODT-derived species with Cu-containing intermetallic regions rather than a homogeneous modification of the entire alloy surface.

Overall, the EIS results indicate that ODPA-containing treatments primarily affect the capacitive properties of the AW2024/electrolyte interface, whereas ODT alone causes only a moderate increase in charge-transfer resistance without substantially changing the effective capacitance. The combined ODPA+ODT treatment shows both a strongly reduced effective capacitance and the highest charge-transfer resistance. This behavior is compatible with the proposed complementary functionalization concept, in which ODPA contributes to an extended hydrophobic interphase across the surface, while ODT may additionally reduce electrochemical

activity at Cu-containing intermetallic regions. However, due to the scatter in R_{ct} , particularly for the combined treatment, this interpretation should be regarded as a qualitative trend rather than as a strictly quantitative ranking of the surface states.

Results of Tafel evaluation of LSV data sets are given in Table 19.

Table 19. Tafel-plot parameters derived from LSV measurements of the Reference and modified AW2024 surfaces. The corrosion potential E_{corr} , corrosion current density i_{corr} , and anodic and cathodic Tafel slopes b_a and b_c were obtained from the polarization curves exemplary shown in Figure 55B. Values are given as mean $\pm$ standard deviation.

Surface state	E_{corr} in mV vs SHE	i_{corr} in $\text{nA} \cdot \text{cm}^{-2}$	b_a in $\text{mV} \cdot \text{dec}^{-1}$	b_c in $\text{mV} \cdot \text{dec}^{-1}$
Reference	-202 ± 74	215 ± 96	236 ± 36	-82 ± 20
ODPA	-73 ± 32	8.9 ± 10.3	164 ± 83	-170 ± 33
ODT	-126 ± 18	114 ± 46	181 ± 18	-145 ± 15
ODPA+ODT	-170 ± 15	25.8 ± 13.2	245 ± 23	-157 ± 31

The Tafel parameters derived from the LSV measurements are summarized in Table 19. The untreated Reference surface exhibits the highest current density, with $i_{corr} = 215 \pm 96 \text{ nA} \cdot \text{cm}^{-2}$. This indicates the highest electrochemical activity among the investigated surface states under the applied chloride-free conditions. All molecularly treated surfaces show lower current densities, demonstrating that the ODPA-, ODT-, and ODPA+ODT-based treatments affect the electrochemical response of AW2024.

The lowest mean current density is obtained for the ODPA-treated surface, with $i_{corr} = 8.9 \pm 10.3 \text{ nA} \cdot \text{cm}^{-2}$. However, the standard deviation exceeds the mean value, indicating a pronounced scatter of the Tafel-derived current densities for this surface state. Therefore, this value should not be interpreted as a statistically robust indication that ODPA provides the strongest electrochemical suppression among all molecular treatments. Rather, the result shows that ODPA treatment can lead to very low current densities under the applied chloride-free conditions, but with considerable variability between individual measurements. This behavior is nevertheless consistent with the dynamic water contact angle measurements and the EIS results, which both indicate the formation of an extended hydrophobic interphase after ODPA treatment.

The ODT-treated surface shows an intermediate current density of $114 \pm 46 \text{ nA} \cdot \text{cm}^{-2}$. Thus, ODT reduces the electrochemical activity compared with the Reference surface, but the effect is less pronounced than for the ODPA-containing treatments. This behavior is consistent with the wettability results, where ODT caused only a moderate increase in water repellency. It is also compatible with the ToF-SIMS results obtained on the AlCu5.9 model alloy, which indicated a preferential localization tendency of ODT-derived species on Cu-containing intermetallic regions rather than a complete functionalization of the entire alloy surface. Accordingly, ODT may reduce the activity of specific Cu-rich domains, but does not appear to generate a continuous hydrophobic interphase across the AW2024 surface.

The combined ODPA+ODT treatment yields an i_{corr} value of $25.8 \pm 13.2 \text{ nA} \cdot \text{cm}^{-2}$, which is clearly lower than that of the Reference and ODT-treated surfaces, but higher than that of the ODPA-only surface. This indicates that the combined treatment strongly reduces the current response during polarization, although the Tafel-derived current density does not follow the same ranking as the charge-transfer resistance obtained from EIS. In the EIS measurements, ODPA+ODT exhibited the highest R_{ct} , suggesting the strongest reduction in near-equilibrium interfacial charge-transfer

processes. The difference between both methods may arise from their different perturbation regimes: EIS probes the interface close to OCP, whereas LSV imposes a progressively increasing polarization and is therefore more sensitive to localized defects, molecular rearrangement, or potential-induced changes in the interphase.

The corrosion potentials further indicate treatment-dependent changes in the electrochemical balance of the surface. The Reference surface exhibits an E_{corr} of -363 ± 74 mV vs. SHE. ODPA treatment shifts E_{corr} markedly in the anodic direction to -234 ± 32 mV vs. SHE, while ODT results in an intermediate value of -287 ± 18 mV vs. SHE. The ODPA+ODT-treated surface shows an E_{corr} of -331 ± 15 mV vs. SHE, closer to that of the Reference surface. These shifts indicate that the molecular treatments do not influence anodic and cathodic partial reactions in the same way. In particular, the anodic shift observed for ODPA is consistent with a strong modification of the surface/electrolyte interface and the suppression of the overall current response.

The Tafel slopes support the interpretation that the molecular treatments affect the cathodic response of the AW2024 surface. The Reference surface exhibits a cathodic slope of $b_c = -82 \pm 20$ mV·dec⁻¹, whereas the ODPA-, ODT-, and ODPA+ODT-treated surfaces show more negative values of -170 ± 33 , -145 ± 15 , and -157 ± 31 mV·dec⁻¹, respectively. The increased absolute cathodic slopes suggest that the molecular treatments hinder cathodic reaction kinetics, which is particularly relevant for AW2024 due to the presence of Cu-containing intermetallic particles that can act as local cathodic sites. The anodic Tafel slopes show less systematic variation, with values of 236 ± 36 mV·dec⁻¹ for the Reference, 164 ± 83 mV·dec⁻¹ for ODPA, 181 ± 18 mV·dec⁻¹ for ODT, and 245 ± 23 mV·dec⁻¹ for ODPA+ODT.

Overall, the LSV/Tafel results indicate that all molecular treatments reduce the electrochemical activity of AW2024 compared with the untreated Reference surface in chloride-free Na₂SO₄ electrolyte. The ODPA-treated surface exhibits the lowest mean i_{corr} , but the high relative scatter of this value limits a robust ranking of the molecular treatments based solely on the Tafel-derived current densities. Nevertheless, the low current densities obtained for the ODPA- and ODPA+ODT-treated surfaces are consistent with the formation of hydrophobic molecular interphases inferred from WCA and EIS. ODT shows a more moderate reduction in current density, in agreement with its less pronounced influence on macroscopic wettability and its more localized interaction with Cu-containing regions suggested by the ToF-SIMS model-alloy analysis.

In addition to the Tafel-derived parameters, the shape and reproducibility of the LSV curves provide further information on the electrochemical behavior of the treated AW2024 surfaces. For this, all LSV curves obtained for each surface (modification) state are shown in Figure S11 in the Supporting Information. Some of these LSV curves exhibit sudden current increases in the anodic potential region. Since the measurements were performed in chloride-free Na₂SO₄ electrolyte, the potential at which a pronounced anodic current increase occurs is not interpreted as a classical chloride-induced pitting potential, but rather as a breakdown-related onset potential (abbreviated as “ E_{bd} ” in Figure S11) under the applied measurement conditions.

The Reference surface exhibits a heterogeneous LSV response with pronounced anodic current increases at an E_{bd} -region between 0.11 and 0.18 V vs. SHE, reflecting the electrochemical activity of the untreated AW2024 surface. The ODPA-treated surface shows a comparatively broad scatter and partially irregular anodic current responses. This indicates that, although ODPA strongly hydrophobizes the surface and reduces the effective capacitance, the interphase may still contain local defects or electrochemically accessible regions that become active during progressive polarization. An E_{bd} is not possible to determine due to the scatter of LSV curves.

In contrast, the ODT-treated surface shows a more uniform polarization behavior than the ODPA-treated surface, although the overall current reduction is less pronounced than for ODPA-containing treatments according to the Tafel analysis. The E_{bd} is at approximately 0.17 mV vs. SHE. This may suggest that ODT affects specific electrochemically active Cu-containing regions, but does not generate the same global hydrophobic interphase as ODPA.

The ODPA+ODT-treated surface exhibits the most reproducible and stable LSV response, with comparatively delayed and less abrupt anodic current increases. The E_{bd} is at approximately 0.16 mV vs. SHE. This behavior is consistent with the EIS results, where the combined treatment showed the highest charge-transfer resistance, and supports the interpretation that the ODPA+ODT treatment combines a globally hydrophobic ODPA-related interphase with an additional ODT-related influence on Cu-containing intermetallic regions.

4.3.5. Conclusion on Complementary ODPA/ODT-Based Functionalization of AW2024

The aim of this section was to evaluate whether a complementary ODPA/ODT-based molecular treatment can address chemically distinct domains of a heterogeneous Al–Cu alloy surface more effectively than a single phosphonic-acid-based modification. This question was motivated by the limited protective effect observed for ODPA-treated AW2024 surfaces under preliminary atmospheric exposure conditions and by the assumption that Cu-containing intermetallic regions may require a molecular functionality different from phosphonic acid anchoring.

The ToF-SIMS analysis of the AlCu5.9 model alloy provided the most direct indication of phase-correlated molecular localization within this section. P^- -related signals, used as indicators for ODPA-derived species, were detected by means of ToF-SIMS on both the Al-rich matrix and the Cu-containing intermetallic regions. Thus, no clear preference of ODPA-derived species for one of the investigated microstructural domains was observed. This finding suggests that phosphonic-acid-related adsorption sites are not restricted to the Al-rich matrix, but may also be present on oxide-covered Cu-containing intermetallic regions. In contrast, S^- -related signals associated with ODT-containing treatments showed a pronounced enrichment on the Cu-containing intermetallic regions. This supports the assumption that ODT-derived species preferentially localize at Cu-rich domains, consistent with the higher affinity of sulfur-containing head groups toward copper-containing surfaces.

The combined ODPA+ODT treatment therefore partly fulfills the conceptual expectation formulated in Section 4.3.1. ODPA-derived species appear to contribute to a more extended molecular modification of the oxide-covered alloy surface, whereas ODT-derived species provide a complementary contribution at Cu-containing intermetallic regions. However, the results do not indicate a strict mutually exclusive self-localization of both molecules. Instead, the data suggest a more complex adsorption behavior governed by the oxide-covered nature of the Al–Cu surface, where ODPA can interact with both investigated surface regions and ODT shows a stronger phase-correlated localization tendency toward Cu-containing domains.

The transfer of the molecular treatment strategy to AW2024 confirmed that the applied treatments modify the overall surface properties of the technical alloy. ODPA-containing treatments produced strongly hydrophobic surfaces and showed spectroscopic signatures consistent with alkyl-chain-containing molecular species. In contrast, ODT treatment alone resulted in a more moderate increase in hydrophobicity and a less pronounced PM-IRRAS

signature, which is consistent with a more localized rather than surface-wide modification. These findings support the interpretation that ODPA primarily governs the macroscopic hydrophobicity of the treated AW2024 surface, while ODT may contribute more specifically to Cu-containing microstructural regions.

The electrochemical measurements performed in chloride-free Na_2SO_4 electrolyte further showed that all molecular treatments influence the interfacial response of AW2024. ODPA-containing treatments strongly affected the capacitive behavior of the interface, consistent with the formation of an extended hydrophobic molecular interphase. ODT alone produced a more moderate electrochemical effect, in line with its proposed localized interaction with Cu-containing regions. The combined ODPA+ODT treatment showed the highest charge-transfer resistance and a comparatively stable response to polarization, indicating that the combination of both molecules can influence complementary aspects of the heterogeneous AW2024 interface. Nevertheless, the electrochemical data should be interpreted as treatment-related changes in interfacial activity under chloride-free conditions, not as a direct prediction of corrosion resistance in chloride-containing environments.

Overall, the results of this section support the central idea that chemically heterogeneous Al–Cu alloy surfaces cannot be fully described by a single-chemistry adsorption concept. A phosphonic-acid-based modification can generate a hydrophobic molecular interphase on AW2024, but it does not specifically address the Cu-containing intermetallic regions that are critical for local electrochemical activity. The addition of ODT provides a complementary chemical functionality that preferentially contributes to these Cu-containing regions, at least on the simplified AlCu5.9 model alloy. However, due to the complexity of the native oxide structures and the limitations of phase-resolved analysis on AW2024, the observed trends should be understood as evidence for phase-correlated adsorption tendencies rather than as definitive proof of selective molecular adsorption on the technical alloy surface. The combined ODPA/ODT approach therefore represents a promising but not yet fully resolved strategy for molecular functionalization of heterogeneous Al–Cu alloy surfaces.

5. Overall Conclusions

The central research question of this dissertation was whether chemically heterogeneous aluminum alloy surfaces can be effectively addressed by a single surface modification chemistry, or whether complementary molecular, polymeric, and inorganic modification strategies are required to account for distinct surface domains within technically relevant microstructures. Based on the results of the three experimental parts of this work, this question can be answered in a differentiated way: single-component modifications can improve specific aspects of the surface and interfacial response, but they are generally insufficient to fully account for the chemical and electrochemical complexity of heterogeneous aluminum alloy surfaces.

5.1. Main findings

For the additively manufactured AlSi10Mg alloy in the as-built condition, PDMS grafting demonstrated that a polymer-based modification can be introduced even onto a rough and chemically inhomogeneous surface. However, the electrochemical improvement remained limited, despite successful spectroscopic verification and increased hydrophobicity. This indicates that macroscopic surface coverage and reduced wettability alone do not necessarily result in complete electrochemical passivation. The subsequent ODPa treatment improved the electrochemical response more strongly, suggesting that residual oxide-covered or electrochemically active surface sites remained accessible after PDMS grafting and could be addressed by a complementary molecular functionality. Thus, the as-built AlSi10Mg study shows that a single polymer-based chemistry can modify the surface, but does not necessarily provide a sufficiently continuous or functionally robust interphase on a highly heterogeneous AM alloy surface.

The investigations on mechanically and chemically pretreated AlSi10Mg further support this conclusion. In this case, the SiO_x-CVD interlayer and the PDMS top layer fulfilled different interfacial functions. The SiO_x-CVD layer primarily improved the electrochemical response in short-term electrolyte measurements, whereas PDMS mainly altered the capacitive behavior, reduced wettability, and improved the response under simulated atmospheric corrosion conditions. The combined SiO_x-CVD+PDMS architecture showed the most robust overall performance because it integrated both effects: electrochemical interfacial stabilization by the inorganic interlayer and wetting-controlled protection by the hydrophobic polymer-derived top layer. This demonstrates that complementary thin-film architectures can provide a more effective strategy than individual surface modifications when different degradation-relevant mechanisms are governed by different interfacial properties.

The AW2024 study extends this concept to a conventionally produced Al–Cu alloy with a different type of chemical heterogeneity. Here, the guiding question was whether phosphonic-acid and thiol head-group chemistries can complement each other by addressing Al-oxide-rich and Cu-containing surface domains, respectively. The ToF-SIMS analysis of the AlCu5.9 model alloy indicated that ODPa-derived species are not restricted to Al-rich regions, but are also detected on Cu-containing intermetallic regions, most likely due to the oxide-covered nature of these domains. In contrast, ODT-derived species showed a stronger localization tendency at Cu-

containing regions. The combined ODPa+ODT strategy therefore does not result in a simple mutually exclusive self-localization of both molecules, but rather in a more complex adsorption behavior in which ODPa contributes to a more extended hydrophobic molecular interphase, while ODT provides an additional Cu-affine functionality. On AW2024, this interpretation is supported by the macroscopic wettability, PM-IRRAS, and electrochemical data, although direct proof of phase-selective adsorption on the technical alloy surface was not achieved.

5.2. Answer to the research question

Across all investigated systems, the results confirm the fundamental assumption that the design of nanometer-scale modification strategies for aluminum alloys must explicitly consider the local substrate chemistry. Chemically heterogeneous alloy surfaces should not be treated as uniform aluminum oxide substrates. Instead, intermetallic phases, Si-rich or Cu-rich regions, spatially varying oxide compositions, and surface pretreatment conditions strongly influence adsorption, grafting, interfacial stability, wettability, and electrochemical response. Consequently, the effectiveness of a surface modification is not defined solely by the nominal chemistry of the applied molecule, polymer, or inorganic layer, but by the compatibility between this chemistry and the locally available surface sites.

The hypothesis that complementary modification strategies can reduce interfacial discontinuities and promote a more functionally robust nanometer-scale interphase is therefore supported by the overall findings of this dissertation. However, this support is not equivalent to proof of ideal homogeneous or perfectly selective surface functionalization. Rather, the results show that complementary approaches improve the probability of addressing different surface domains and different protection-relevant functions. In this sense, the most successful strategies were not those based on a single universal anchoring chemistry, but those combining different interfacial functions, such as oxide-specific molecular adsorption, polymer-based hydrophobization, inorganic interlayer formation, and Cu-affine molecular interaction.

Thus, the work bridges the gap between classical surface functionalization concepts developed for idealized aluminum, silicon oxide, or copper model surfaces and the requirements of chemically heterogeneous engineering alloys. It demonstrates that nanometer-scale surface modifications can be adapted to alloy-specific surface heterogeneity, but also that their interpretation requires careful distinction between global surface modification, local adsorption tendencies, and functional electrochemical response. The central conclusion is therefore that chemically tailored, multifunctional interfacial engineering provides a more realistic and effective design principle for corrosion-related surface modification of aluminum alloys than single-chemistry approaches applied without consideration of the underlying microstructure.

5.3. Critical assessment of nanometer-scale thin film strategies for aluminum alloys

The results of this dissertation demonstrate that nanometer-scale surface modifications can provide valuable interfacial design tools for chemically heterogeneous aluminum alloys. Their

main advantage is that they modify the outermost surface region without fundamentally altering the bulk alloy composition, the microstructure, or the macroscopic geometry of the component. This is particularly relevant for aluminum alloys, where corrosion processes are initiated at the interface between the native oxide, local intermetallic phases, adsorbed electrolyte, and the surrounding environment. By tailoring this interfacial region, molecular, polymeric, and inorganic thin films can influence wettability, adsorption behavior, charge-transfer processes, and the accessibility of electrochemically active surface sites. In addition, nanometer-scale modification strategies can offer potential advantages in terms of material efficiency, low coating thickness, reduced resource consumption, and the use of comparatively mild process conditions or less hazardous chemistries, which are becoming increasingly important criteria in future surface engineering approaches.

Within this work, the investigated modification strategies contributed different interfacial functions. ODPA-based treatments were effective in generating hydrophobic, alkyl-terminated surfaces and in modifying oxide-covered alloy interfaces. ODT introduced a Cu-affine molecular functionality that was particularly relevant for Cu-containing intermetallic regions, as indicated by the AlCu5.9 model-alloy experiments. PDMS provided a hydrophobic polymer-derived top layer, whereas SiO_x-CVD acted as an inorganic interlayer capable of improving electrochemical interfacial stabilization. The combination of such functionalities illustrates the central conceptual advantage of multifunctional thin-film strategies: instead of relying on a single protective mechanism, different degradation-relevant aspects of the alloy/electrolyte or alloy/atmosphere interface can be addressed simultaneously.

However, the results also reveal fundamental limitations of nanometer-scale thin-film strategies on complex aluminum alloy surfaces. Self-assembly-based approaches are intrinsically governed by adsorption equilibria, local surface chemistry, oxide structure, hydroxylation state, solvent interactions, contamination, and surface pretreatment. As the chemical and microstructural complexity of the substrate increases, the controlled and reproducible formation of a targeted molecular layer becomes increasingly difficult. On idealized substrates, selective adsorption concepts can often be interpreted more clearly because the number of competing surface sites is limited. On technical alloys, however, multiple oxide chemistries, intermetallic phases, and local electrochemical environments coexist within small lateral length scales. This can lead to incomplete coverage, locally different adsorption states, defect formation, and reduced reproducibility.

This limitation is particularly relevant for strategies that aim to address specific microstructural domains through complementary head-group chemistries. The ODPA/ODT concept investigated in this work illustrates both the potential and the difficulty of such an approach. On the AlCu5.9 model alloy, ODT-derived species showed a phase-correlated localization tendency toward Cu-containing regions, whereas ODPA-derived species were detected on both investigated microstructural regions. This demonstrates that complementary molecular functionalities can influence different surface domains, but also that adsorption is not governed by a simple one-molecule/one-phase relationship. The oxide-covered nature of technical alloy surfaces complicates the direct translation of idealized adsorption preferences to real engineering alloys. Consequently, complementary functionalization should be understood as a strategy to increase the likelihood of addressing different surface domains, rather than as a guarantee of perfectly selective molecular self-localization.

A further limitation concerns the protective function of nanometer-scale films under aggressive electrolyte exposure. The thin films investigated in this dissertation are not classical barrier

coatings with sufficient thickness to provide long-term physical separation between the alloy and a corrosive medium. Instead, their protective contribution arises from interfacial modification: reduced wettability, altered dielectric properties, hindered charge transfer, changed adsorption behavior, or reduced accessibility of local electrochemically active sites. Under chloride-containing immersion conditions, such nanometer-scale modifications can therefore only provide limited short-term protection, especially when defects, intermetallic particles, or residual conductive pathways remain accessible to the electrolyte.

In contrast, the investigated thin-film strategies appear more suitable for influencing atmospheric corrosion processes, where surface wetting, electrolyte film formation, droplet stability, and local ion accumulation play a central role. Under such conditions, even very thin hydrophobic or chemically modified interphases can affect the formation and persistence of electrolyte layers and thereby modify the onset or progression of corrosion-related processes. The improved behavior of the combined SiO_x -CVD+PDMS system under simulated atmospheric exposure supports this interpretation. In this case, the protective effect is likely not only related to a barrier function, but also to physicochemical changes of the outer interface, including reduced water interaction and modified electrolyte accessibility.

Nevertheless, the preliminary atmospheric corrosion experiments on ODP-treated AW2024 also demonstrate that such effects cannot be generalized across all alloy systems and exposure conditions. For this particularly challenging Al–Cu alloy, ODP treatment did not lead to a clearly discernible suppression of local corrosion events under the applied high-humidity NaCl exposure. This does not necessarily contradict the beneficial wetting and electrochemical effects observed under other conditions, but it highlights that highly localized corrosion processes at Cu-containing intermetallic regions may not be sufficiently controlled by a phosphonic-acid-based modification alone. In addition, the high relative humidity and the deliquescence of deposited NaCl particles resulted in electrolyte droplet formation, thereby creating a locally aggressive exposure scenario. Under such conditions, nanometer-scale molecular films may be rapidly challenged by concentrated electrolyte droplets, local galvanic coupling, and passive-film destabilization.

Taken together, nanometer-scale thin-film strategies should therefore not be interpreted as stand-alone replacements for robust corrosion protection coatings under severe chloride exposure. Their strength lies instead in the targeted modification of the alloy/environment interface and in the possibility of combining different interfacial functions. They are particularly valuable for reducing initial interfacial activity, controlling wetting behavior, modifying local adsorption processes, and improving the early-stage response under moderately aggressive or atmospheric conditions. For long-term corrosion protection in chloride-rich environments, however, such modifications would likely need to be integrated into more robust multilayer or hybrid protection systems that combine nanometer-scale interfacial control with thicker, mechanically stable, and defect-tolerant barrier layers.

The critical implication of this work is therefore that nanometer-scale surface modifications are most effective when their function is defined realistically. They can tailor and stabilize specific aspects of the interfacial response, but they cannot fully compensate for the intrinsic electrochemical complexity of highly heterogeneous aluminum alloys. The most promising strategies are those that combine substrate-specific interfacial chemistry with complementary protective functions and that explicitly account for the local microstructural and chemical heterogeneity of the alloy surface.

5.4. Methodological implications

A central methodological implication of this dissertation is that the characterization of nanometer-scale modifications on chemically heterogeneous aluminum alloys requires a combination of complementary analytical and electrochemical techniques. No single method applied in this work was sufficient to fully answer the research question on its own. Instead, the individual methods provided different levels of information, ranging from integral surface chemistry and macroscopic physicochemical properties to electrochemical functionality and phase-correlated chemical localization. The interpretation of the results therefore relies on the combined assessment of global surface modification, local alloy heterogeneity, and functional interfacial response.

XPS and PM-IRRAS provided highly surface-sensitive information on the chemical composition and molecular structure of the modified surfaces. XPS was particularly useful for identifying treatment-induced changes in elemental composition and chemical bonding states, whereas PM-IRRAS enabled the detection of characteristic vibrational features associated with alkyl-chain-containing surface species and their apparent conformational order. These methods were therefore essential for verifying that the applied molecular, polymeric, or inorganic treatments modified the outermost surface region. However, in the way they were applied in this thesis, both methods provided predominantly integral information over the analyzed surface area. They therefore could not directly demonstrate whether the observed chemical changes resulted from homogeneous surface coverage, localized adsorption at specific microstructural domains, or a combination of both. Consequently, XPS and PM-IRRAS were highly valuable for confirming surface modification, but not sufficient to prove phase-selective adsorption processes on heterogeneous alloy surfaces.

Nevertheless, XPS may provide additional contributions to this question in future studies if more advanced and specifically designed analysis strategies are applied. Spatially resolved XPS, angle-resolved XPS, carefully selected model substrates, or systematic depth-profiling approaches could help to differentiate between chemically distinct surface regions or adsorption states. However, such analyses require substantially higher experimental effort, careful calibration, and considerable expertise in both measurement design and data interpretation. Within the scope of the present work, XPS was therefore used primarily as an integral surface-chemical method rather than as a tool for proving lateral adsorption selectivity.

Water contact angle measurements provided complementary information on the physicochemical properties of the investigated surfaces. Static and dynamic contact angle data allowed the influence of the surface modifications on macroscopic wettability to be assessed and provided qualitative evidence for the formation of hydrophobic outer interfaces. In particular, the strong increase in contact angle after ODP- or PDMS-containing treatments supported the successful introduction of alkyl-terminated or polymer-derived surface species. Dynamic contact angle measurements additionally provided information on contact angle hysteresis, which can be affected by chemical heterogeneity, surface roughness, and contact-line pinning. In principle, such measurements can therefore provide semi-quantitative indications of surface heterogeneity. However, in the ODP/ODT study on AW2024, dynamic contact angle measurements did not provide direct evidence for phase-selective adsorption. The method lacks the lateral and chemical resolution required to assign wetting behavior to individual intermetallic particles or alloy phases. Thus, WCA measurements were highly useful for evaluating the macroscopic physicochemical effect of the modifications, but not for resolving their local adsorption behavior.

SEM, EDS, AFM, and SKPFM contributed to the characterization of the topographical, chemical, and electronic heterogeneity of the alloy surfaces. SEM and EDS were important for identifying microstructural features, intermetallic particles, and local compositional differences. However, due to the nanometer-scale thickness of the investigated surface modifications and the limited surface sensitivity of EDS, these methods are not suitable for detecting local adsorption preferences of molecular thin films. Their main contribution was therefore the identification and assignment of relevant substrate heterogeneities rather than the direct detection of the modifications themselves.

AFM and SKPFM offer, in principle, the lateral and height resolution required to probe nanoscale surface features and local variations in surface potential. These methods are therefore highly attractive for investigating the relationship between microstructure, topography, and local electrochemical activity. However, their quantitative interpretation becomes challenging when applied to technically relevant aluminum alloy surfaces. The surface roughness introduced by mechanical or chemical pretreatments, together with the intrinsic topographical and chemical heterogeneity of the substrates, strongly affects the measured height and potential signals. Under the atmospheric measurement conditions used in this work, reliable and reproducible surface-potential differences attributable specifically to the nanometer-scale modifications could not be established. Consequently, AFM and SKPFM provided valuable information on local surface morphology and microstructural heterogeneity, but did not allow a robust quantitative proof of selective adsorption or modification-induced local potential changes.

The electrochemical methods applied in this thesis, including EIS, LSV, and chronoamperometry, were essential for evaluating the functional response of the modified alloy/electrolyte interfaces. EIS provided information on charge-transfer resistance, capacitive behavior, and non-ideal interfacial properties, whereas LSV and chronoamperometry enabled the assessment of potential-dependent electrochemical activity and time-dependent current responses. These techniques were therefore crucial for determining whether the applied modifications improved the electrochemical stability or barrier-related properties of the surfaces. However, the electrochemical response was measured over electrode areas that contained numerous microstructural domains and intermetallic particles. As a result, the obtained data represent integral interfacial responses rather than phase-specific electrochemical information. Under these conditions, electrochemical methods can reveal whether a modification affects the overall surface response, but they cannot directly prove whether this effect originates from selective adsorption on specific phases. A more phase-specific electrochemical assessment would require strongly reduced electrode areas, for example by using microdroplet cells or localized electrochemical techniques capable of probing individual intermetallic particles or selected alloy regions.

Atmospheric corrosion experiments provided an additional functional perspective with high technical relevance. These tests allowed the modified surfaces to be evaluated under exposure conditions closer to realistic atmospheric corrosion scenarios, where electrolyte film formation, droplet stability, humidity, and salt loading play important roles. The results therefore provided qualitative indications of the potential corrosion-inhibiting effect of the applied modifications under atmospheric conditions. However, similar to the conventional electrochemical measurements, these experiments provide predominantly integral or phenomenological information. They reveal whether corrosion-related surface changes are delayed, reduced, or altered, but they do not directly identify the local adsorption state of the applied molecules or polymers. Furthermore, localized corrosion events on heterogeneous alloys can be dominated by

individual intermetallic particles, defects, or local electrolyte conditions, which complicates the direct correlation between surface modification and corrosion response. Nevertheless, the atmospheric corrosion experiments were important because they linked the physicochemical and electrochemical findings to exposure conditions of practical relevance.

Among the methods applied in this work, ToF-SIMS provided the highest potential for addressing the phase-related adsorption question directly. The method combines high surface sensitivity with chemical specificity and lateral resolution, allowing molecularly derived fragment signals to be correlated with microstructural regions. In the AlCu5.9 model-alloy study, ToF-SIMS enabled the evaluation of ODP- and ODT-related secondary ion signals within predefined Al-rich matrix and Cu-containing intermetallic-region ROIs. This provided the strongest evidence for phase-correlated molecular localization obtained in this dissertation. In particular, the ODT-related signal enrichment at Cu-containing regions could not have been resolved by the way methods such as XPS, PM-IRRAS, WCA, or conventional electrochemical measurements has been applied.

However, ToF-SIMS also has important limitations. Secondary ion intensities are strongly affected by local matrix effects, surface chemistry, roughness, sputter behavior, and the selected fragment assignment. Therefore, ToF-SIMS data should not be interpreted as directly quantitative surface coverages without careful calibration and validation. In addition, the method requires substantial expertise in experimental design, data acquisition, depth profiling, ROI definition, and spectral interpretation. Measurement time and data evaluation effort are also considerable, especially when statistically robust phase-resolved analyses are required. For this reason, the ToF-SIMS investigation was performed on a simplified AlCu5.9 model alloy rather than directly on the full microstructural complexity of AW2024. While this approach provided valuable mechanistic insight, it also highlights the limited direct transferability from model systems to technical alloys.

Overall, the methodological findings of this dissertation show that different techniques address different parts of the research question. XPS, PM-IRRAS, and WCA confirmed global chemical and physicochemical surface modification; SEM, EDS, AFM, and SKPFM characterized the microstructural, topographical, and electronic heterogeneity of the substrates; EIS, LSV, chronoamperometry, and atmospheric corrosion experiments evaluated the functional interfacial response; and ToF-SIMS provided the most direct evidence for phase-correlated adsorption tendencies. The central methodological conclusion is therefore that chemically heterogeneous aluminum alloy surfaces cannot be adequately understood through integral surface analysis or global electrochemical testing alone. A reliable assessment of nanometer-scale modification strategies requires the deliberate combination of surface-sensitive chemical analysis, localized microstructural characterization, and functional corrosion-related testing.

This has direct implications for future studies. To establish a more definitive link between local adsorption, microstructural phase identity, and corrosion activity, future methodological approaches should combine spatially resolved chemical analysis with localized electrochemical measurements on well-defined model and technical alloy surfaces. In particular, ToF-SIMS, spatially resolved XPS, microdroplet-cell electrochemistry, localized impedance methods, and carefully designed atmospheric corrosion tests could provide a more direct correlation between molecular localization and functional corrosion response. Such approaches would help to further close the gap between integral evidence of surface modification and direct proof of phase-specific interfacial functionality.

6. Outlook

6.1. Future corrosion-related validation of complementary modification strategies

The results of this dissertation demonstrate that nanometer-scale molecular, polymeric, and inorganic surface modifications can substantially influence the interfacial response of chemically heterogeneous aluminum alloys. However, the extent to which these interfacial changes translate into robust corrosion protection depends strongly on the alloy system, the surface state, and the exposure conditions. Therefore, future work should first focus on the corrosion-related validation of the modification strategies investigated in Section 4 before extending them toward broader technological applications.

A particularly important next step concerns the electrochemical evaluation of the ODPA-, ODT-, and ODPA+ODT-treated AW2024 surfaces under chloride-containing conditions. In this dissertation, the electrochemical response of these surfaces was investigated in chloride-free Na₂SO₄ electrolyte in order to assess treatment-related differences under less aggressive conditions and to minimize rapid chloride-induced degradation during the measurement. These experiments showed that the molecular treatments affect the interfacial charge-transfer resistance, capacitive behavior, and polarization response. However, they do not yet allow a reliable conclusion regarding the corrosion resistance of the treated AW2024 surfaces under chloride exposure. Since localized corrosion of AW2024 is strongly associated with chloride-induced activation of Cu-containing intermetallic regions, future EIS, LSV, and chronoamperometric measurements should be performed in chloride-containing electrolytes to determine whether the observed interfacial effects remain relevant under more corrosion-critical conditions.

Such experiments should compare the Reference, ODPA-, ODT-, and ODPA+ODT-treated surfaces under identical chloride-containing exposure conditions. This would clarify whether the combined ODPA+ODT treatment provides a measurable advantage over the single-molecule treatments when local chloride-induced corrosion processes become dominant. In particular, it should be investigated whether the increased charge-transfer resistance observed for ODPA+ODT in chloride-free electrolyte is retained in chloride-containing solution, or whether defects, local galvanic coupling, and rapid electrolyte access to intermetallic regions override the beneficial interfacial effects of the molecular treatment. This distinction is essential for evaluating whether the complementary SAM concept provides true corrosion-inhibiting functionality or primarily modifies the electrochemical response under comparatively mild conditions.

In addition to conventional electrochemical measurements, the atmospheric corrosion experiments should be repeated and extended. The preliminary NaCl/high-humidity exposure tests on ODPA-treated AW2024 did not reveal a clearly discernible suppression of local corrosion events compared with the untreated Reference surface. However, these experiments were limited in scope and did not include the combined ODPA+ODT treatment. Future atmospheric corrosion studies should therefore systematically compare all relevant surface states, including ODPA, ODT, and ODPA+ODT, under well-controlled humidity, salt-loading, and exposure-time conditions. Such experiments would allow the complementary adsorption concept to be

evaluated under conditions that are more representative of atmospheric corrosion initiation than full immersion tests.

A key aspect of future atmospheric corrosion testing should be the distinction between electrolyte immersion, deliquescent salt droplet exposure, and thin electrolyte film formation. The high relative humidity used in the preliminary AW2024 experiments promoted the deliquescence of deposited NaCl particles and the formation of localized electrolyte droplets. Under these conditions, the molecular films are exposed to highly concentrated electrolyte environments at specific surface sites, which may strongly challenge their stability and protective function. Future studies should therefore include a systematic variation of relative humidity, salt loading, and wet/dry cycling in order to determine under which atmospheric conditions nanometer-scale modifications can meaningfully influence corrosion initiation. This is particularly relevant because such films are expected to be more effective in controlling wetting, electrolyte film stability, and early-stage interfacial processes than in providing long-term barrier protection under continuous chloride immersion.

The combined SiO_x-CVD+PDMS system investigated on AlSi10Mg also warrants further corrosion-related validation. The results of this dissertation indicated that the inorganic interlayer and the polymer-derived top layer contribute different protective functions, with the combined system showing the most robust overall response under the investigated conditions. Future work should therefore examine the long-term stability of this multilayer architecture under repeated humidity exposure, wet/dry cycling, and chloride-containing atmospheric environments. In particular, it should be clarified whether the improved atmospheric corrosion behavior is governed primarily by reduced wettability, enhanced interfacial impedance, improved defect tolerance, or a combination of these effects.

For both alloy systems, future corrosion validation should also address the durability of the nanometer-scale modifications themselves. Molecular and polymer-derived interphases may undergo hydrolysis, desorption, oxidation, rearrangement, or contamination during exposure. Therefore, corrosion testing should be combined with post-exposure surface analysis in order to determine whether changes in electrochemical behavior are caused by stable protection, partial degradation of the modification, or transformation of the native oxide/interphase structure. Techniques such as XPS, PM-IRRAS, WCA, and ToF-SIMS could be applied before and after exposure to correlate functional performance with chemical and structural changes of the modified interface.

Overall, the next experimental step should be to test whether the interfacial effects identified in this dissertation persist under more corrosion-relevant conditions. For AW2024, this requires chloride-containing electrochemical measurements and systematic atmospheric corrosion tests including the combined ODPA+ODT treatment. For AlSi10Mg, the long-term performance of SiO_x-CVD-, PDMS-, and combined SiO_x-CVD+PDMS-modified surfaces should be evaluated under cyclic atmospheric exposure. Such studies would allow the distinction between short-term interfacial stabilization, wetting-controlled corrosion inhibition, and durable corrosion protection to be made more clearly. They would also provide a more robust basis for judging whether complementary nanometer-scale modification strategies can contribute to technically relevant corrosion protection concepts for heterogeneous aluminum alloys.

6.2. Correlative approaches for phase-specific adsorption and local electrochemical functionality

A central open question arising from this dissertation is whether the phase-correlated adsorption tendencies observed on heterogeneous aluminum alloy surfaces directly translate into a local reduction of electrochemical activity. The ToF-SIMS investigation of the AlCu5.9 model alloy provided evidence that ODT-derived species preferentially localize at Cu-containing intermetallic regions, whereas ODPA-derived species are detected on both the Al-rich matrix and the Cu-containing regions. However, ToF-SIMS primarily provides chemical information and does not directly show whether the local electrochemical behavior of these microstructural domains is altered by the molecular treatment. A logical next step would therefore be to combine phase-resolved chemical analysis with localized electrochemical measurements.

The AlCu5.9 model alloy investigated in this work would be particularly suitable for such a follow-up study. Its simplified Al–Cu microstructure, consisting of an Al-rich matrix and Cu-containing intermetallic regions, provides a more interpretable system than technically more complex alloys such as AW2024. Future studies could apply scanning electrochemical microscopy (SECM) to the same set of surface states investigated by ToF-SIMS, namely Reference, ODPA, ODT, and ODPA+ODT. In this way, the local electrochemical activity of Al-rich and Cu-containing regions could be compared before and after the different molecular treatments.

Such an approach would allow the ODPA/ODT concept to be evaluated from a functional perspective. If ODT-derived species preferentially localize at Cu-containing intermetallic regions, SECM could help to determine whether these regions also exhibit reduced local electrochemical activity after ODT or ODPA+ODT treatment. Similarly, it could be investigated whether ODPA treatment primarily affects the oxide-covered alloy surface more generally, rather than selectively suppressing the activity of Cu-containing regions. The combined ODPA+ODT treatment would be of particular interest, because it may produce a more balanced modification of both the Al-rich matrix and Cu-containing intermetallic regions. A reduced contrast in local electrochemical activity between both regions after combined treatment would provide strong support for the functional relevance of complementary molecular functionalization.

In this context, SECM should be regarded as a method for probing local electrochemical functionality rather than as a direct chemical proof of adsorption. The chemical localization of the molecular species would still need to be evaluated by surface-sensitive techniques such as ToF-SIMS or, where applicable, advanced XPS approaches. The strength of SECM would lie in its ability to determine whether chemically modified regions exhibit altered local redox activity or charge-transfer behavior. A correlative workflow combining ToF-SIMS and SECM on comparable or identical surface regions would therefore be highly valuable. ToF-SIMS could identify where ODPA- and ODT-derived species are located, whereas SECM could determine whether these local chemical differences are accompanied by changes in electrochemical activity.

Microdroplet-cell approaches could provide an additional or complementary route to this question. By reducing the electrolyte contact area to selected microstructural domains, individual Al-rich or Cu-containing regions could be electrochemically probed more selectively than in conventional macroscopic EIS or LSV measurements. Such measurements would make it possible to compare the electrochemical response of defined phase regions before and after molecular treatment. Although the spatial resolution of microdroplet cells is typically lower than

that of high-resolution scanning techniques, their advantage lies in the possibility of applying conventional electrochemical protocols to locally confined surface areas. This could bridge the gap between global electrochemical measurements and highly localized scanning methods.

A similar localized electrochemical strategy would also be highly relevant for the AlSi10Mg systems investigated in this dissertation. In Sections 4.1 and 4.2, PDMS-, SiO_x-CVD-, and combined SiO_x-CVD+PDMS-based modification strategies were shown to influence the macroscopic wettability and electrochemical response of additively manufactured AlSi10Mg surfaces. However, the local contribution of different microstructural regions, such as Al-rich matrix areas, Si-rich domains, and oxide-modified surface regions, remains unresolved. SECM or related localized electrochemical techniques could be applied to polished and etched AlSi10Mg substrates with and without SiO_x-CVD, PDMS, and combined SiO_x-CVD+PDMS modifications. This would help to determine whether the improved interfacial response observed for the combined system originates from a more homogeneous suppression of local electrochemical activity or from the stabilization of specific reactive surface domains.

For both AlCu5.9 and AlSi10Mg, future studies should ideally follow a correlative experimental workflow. First, the microstructure should be identified by SEM/EDS, AFM, or related imaging methods. Second, the local distribution of molecule- or layer-related species should be assessed by ToF-SIMS or advanced surface analysis. Third, localized electrochemical techniques such as SECM or microdroplet-cell measurements should be applied to evaluate the electrochemical activity of the same or comparable regions. Finally, controlled atmospheric corrosion exposure and post-exposure analysis could determine whether local chemical modification and reduced electrochemical activity translate into delayed corrosion initiation.

Such a correlative strategy would directly address one of the central limitations of the present dissertation: the separation between chemical evidence of surface modification and functional evidence of corrosion-related interfacial stabilization. While global methods demonstrated that the investigated modifications alter the overall surface and electrochemical response, they could not prove which local surface regions are responsible for these effects. Future SECM- and microdroplet-based studies on well-defined model alloys and selected technical substrates could therefore provide a much stronger link between phase-specific adsorption, local electrochemical activity, and corrosion inhibition.

Overall, the most promising future research direction is not the isolated application of additional characterization methods, but the deliberate combination of spatially resolved chemical and electrochemical techniques. For the ODP/ODT concept, this would allow the proposed complementary adsorption behavior to be tested not only chemically, but also functionally. For the SiO_x-CVD/PDMS strategy on AlSi10Mg, it would help to identify how inorganic and polymer-derived interfacial layers influence local electrochemical activity across heterogeneous alloy surfaces. Such studies would substantially strengthen the mechanistic understanding of complementary nanometer-scale modification strategies and provide a more robust basis for their future development.

6.3. Future potential of complementary nanometer-scale interfacial strategies

Beyond the corrosion-related validation and localized methodological approaches discussed above, the results of this dissertation also suggest broader application perspectives for complementary nanometer-scale interfacial strategies.

The results of this dissertation indicate that nanometer-scale surface modifications should not be regarded as direct replacements for conventional corrosion protection systems, such as thicker organic coatings, conversion layers, anodic oxide layers, or multilayer barrier systems. The molecular, polymeric, and inorganic thin films investigated in this work are too thin to provide long-term physical separation between aluminum alloys and aggressive chloride-containing electrolytes. Their protective effect is instead based on the modification of the outermost interfacial region, including changes in wettability, surface chemistry, dielectric behavior, adsorption properties, and local charge-transfer processes. Consequently, their future potential lies less in their use as stand-alone corrosion protection coatings under severe immersion conditions and more in their function as chemically tailored interfacial layers within more complex surface engineering concepts.

This distinction is important for evaluating the technological relevance of the approaches investigated in this work. Under long-term chloride immersion, nanometer-scale molecular or polymeric films are likely to be rapidly challenged by defects, local electrolyte access, intermetallic particles, and galvanically driven degradation pathways. In such environments, more robust barrier-forming protection strategies are required. However, the studies presented in this dissertation suggest that nanometer-scale modifications can be highly relevant for controlling the initial interaction between a chemically heterogeneous aluminum alloy surface and its environment. This is particularly important under atmospheric exposure conditions, where surface wetting, electrolyte droplet formation, humidity-dependent adsorption processes, and local salt accumulation strongly influence corrosion initiation.

The concept of complementary nanometer-scale functionalization is especially promising because it explicitly considers the chemical heterogeneity of technical aluminum alloys. Instead of relying on a single anchoring chemistry, future strategies could combine different molecular functionalities that interact preferentially with different surface domains. In this way, the overall interfacial coverage, chemical continuity, or functional robustness of the modified surface may be improved. The results obtained for the ODPA/ODT system support this concept at least at the level of phase-correlated adsorption tendencies on the AlCu5.9 model alloy. Although ideal selective self-localization was not demonstrated, the combined approach showed that different head-group chemistries can contribute differently to the modification of a heterogeneous Al–Cu surface.

A particularly relevant future direction is the use of complementary adsorption systems as adhesion-promoting interphases rather than as corrosion protection layers in their own right. Even if nanometer-scale films do not provide durable corrosion protection under aggressive electrolyte exposure, they may improve the chemical coupling between an alloy substrate and a subsequently applied coating, adhesive, or hybrid protection system. This would shift their function from direct barrier protection toward interfacial engineering. In this context, complementary adsorption strategies could be used to increase the number of chemically

coupled surface sites across heterogeneous alloy surfaces and thereby improve the adhesion, durability, and interfacial stability of subsequent macroscopic protection systems.

Such an approach is particularly attractive for self-assembled molecules because their molecular architecture can, in principle, be designed independently at the substrate-binding and outward-facing ends. The anchoring group can be selected to interact with specific surface chemistries, such as oxide-rich aluminum regions or Cu-containing intermetallic domains, while the terminal functional group can be chosen to interact with a coating or adhesive system. For example, amine-, hydroxyl-, epoxy-, or carboxyl-terminated molecules could be considered as coupling layers for epoxy-based adhesives or organic coatings. In this way, complementary molecular systems could serve as phase-adapted adhesion promoters on chemically heterogeneous aluminum alloys.

This perspective is highly relevant for adhesively bonded aluminum structures. In such systems, failure often initiates at or near the substrate/adhesive interface, especially under humid or corrosive conditions. A nanometer-scale interphase that improves chemical coupling between the alloy surface and the adhesive may therefore contribute to enhanced long-term durability, even if the molecular layer itself does not act as a robust corrosion barrier. Future studies could therefore investigate whether complementary SAM-based treatments improve the durability of aluminum/epoxy adhesive joints under combined mechanical and corrosive loading. This would provide a direct technological extension of the phase-specific functionalization concept developed in this dissertation.

Beyond adhesive bonding, complementary nanometer-scale interphases could also serve as molecular primers for subsequent coating systems. By improving the chemical compatibility between the heterogeneous alloy surface and a sol-gel coating, polymer coating, or hybrid barrier layer, they may enhance coating adhesion and reduce interfacial defect formation. In this role, the nanometer-scale modification would act as a chemically adaptive coupling layer between the complex alloy surface and a more robust macroscopic protection system. Such multilayer concepts could combine the advantages of nanoscale interfacial control with the mechanical stability and defect tolerance of thicker coatings.

PDMS-based surface modification represents a different but equally relevant future direction. In contrast to SAM molecules, PDMS does not offer the same degree of molecular design flexibility with respect to terminal functional groups for adhesion promotion. Its main potential lies instead in its hydrophobizing character, low surface energy, broad availability, comparatively simple processing, and generally low acute toxicity. The results of Sections 4.1 and 4.2 showed that PDMS-based grafting can be applied to metal-oxide-covered surfaces and can strongly affect wettability and electrochemical interfacial behavior. However, PDMS should not be considered a stand-alone long-term corrosion protection layer under aggressive chloride exposure. Its more realistic potential lies in applications where reduced water interaction, delayed electrolyte wetting, or low surface energy are beneficial.

One promising application field for PDMS-based treatments is the generation of highly water-repellent or potentially superhydrophobic surfaces on substrates with suitable roughness. Since superhydrophobicity requires both low surface energy and appropriate surface texture, rough aluminum surfaces or additively manufactured substrates may provide favorable starting points for such approaches. In this context, PDMS could be used as a comparatively simple hydrophobizing reagent to exploit existing surface roughness rather than to create a thick protective coating. This may be particularly relevant for atmospheric exposure conditions, where

reduced droplet adhesion, modified wetting behavior, and delayed electrolyte film formation can influence corrosion initiation.

The UV-induced PDMS grafting approach investigated in this work may be especially interesting from a processing perspective because it allows comparatively rapid surface modification. This could be advantageous for technical implementation if short treatment times are required. However, the need for UV irradiation also introduces practical limitations, since large-scale application would require suitable UV-transparent process environments or industrial treatment systems equipped with UV illumination. Compared with water-induced grafting approaches, this adds process complexity and may increase equipment costs. Nevertheless, the reduced treatment time may compensate for these disadvantages in specific applications, particularly if the process can be integrated into continuous or automated surface treatment lines.

Future development of PDMS-based strategies should also include a more detailed assessment of environmental persistence, degradability, and end-of-life behavior of silicone-based surface species. Although PDMS is widely used, comparatively inexpensive, and generally considered to have low acute toxicity, its long-term environmental fate should be carefully considered when proposing it as a broad surface engineering material. Thus, future studies should evaluate not only the functional performance of PDMS-modified surfaces, but also their durability, aging behavior, removability, and sustainability under realistic service and processing conditions.

Overall, the future potential of nanometer-scale surface modification strategies lies in their targeted use as interfacial design elements rather than as universal corrosion protection coatings. Complementary SAM-based systems may be particularly valuable as chemically adaptive adhesion-promoting layers for heterogeneous aluminum alloys, while PDMS-based approaches may be useful for hydrophobization and wetting control, especially under atmospheric exposure conditions. The most promising future concepts will likely combine nanometer-scale interfacial functionalization with more robust macroscopic protection systems. In such hybrid architectures, the nanoscale layer would provide chemical coupling, wetting control, or local interfacial stabilization, while the overlying coating or adhesive would provide mechanical integrity and long-term barrier protection.

7. Supporting Information

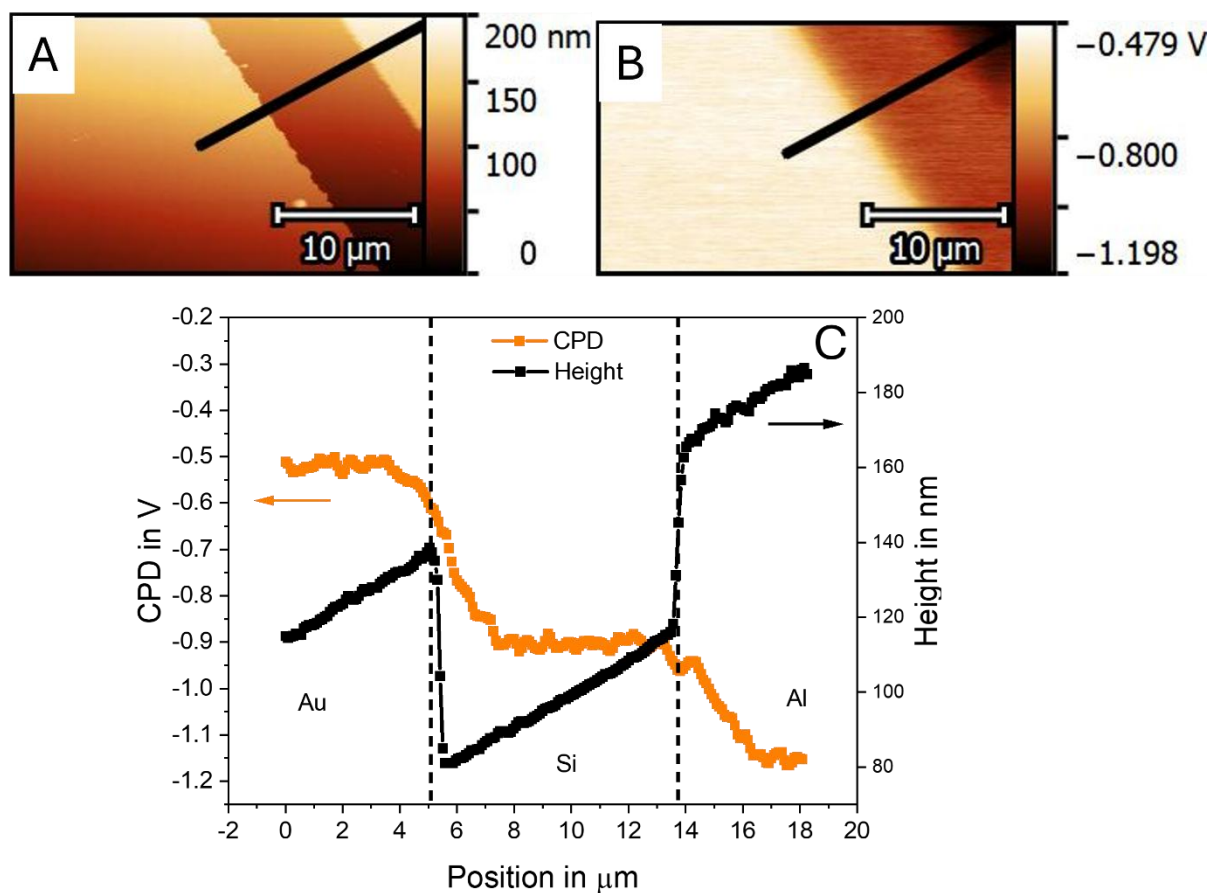


Figure S1. FM-SKPFM measurement of the Bruker test sample "PFKPFM-SMPL". The measurement was performed using a "SCM-PIT-V2" cantilever. (A) AFM height image with the indicated line profile. (B) Corresponding contact potential difference (CPD) image recorded on the same area, with the line profile indicated. (C) Combined height and CPD line profiles extracted along the marked positions in (A) and (B). The investigated material regions, namely Au, Si, and Al, are indicated in the line profile.

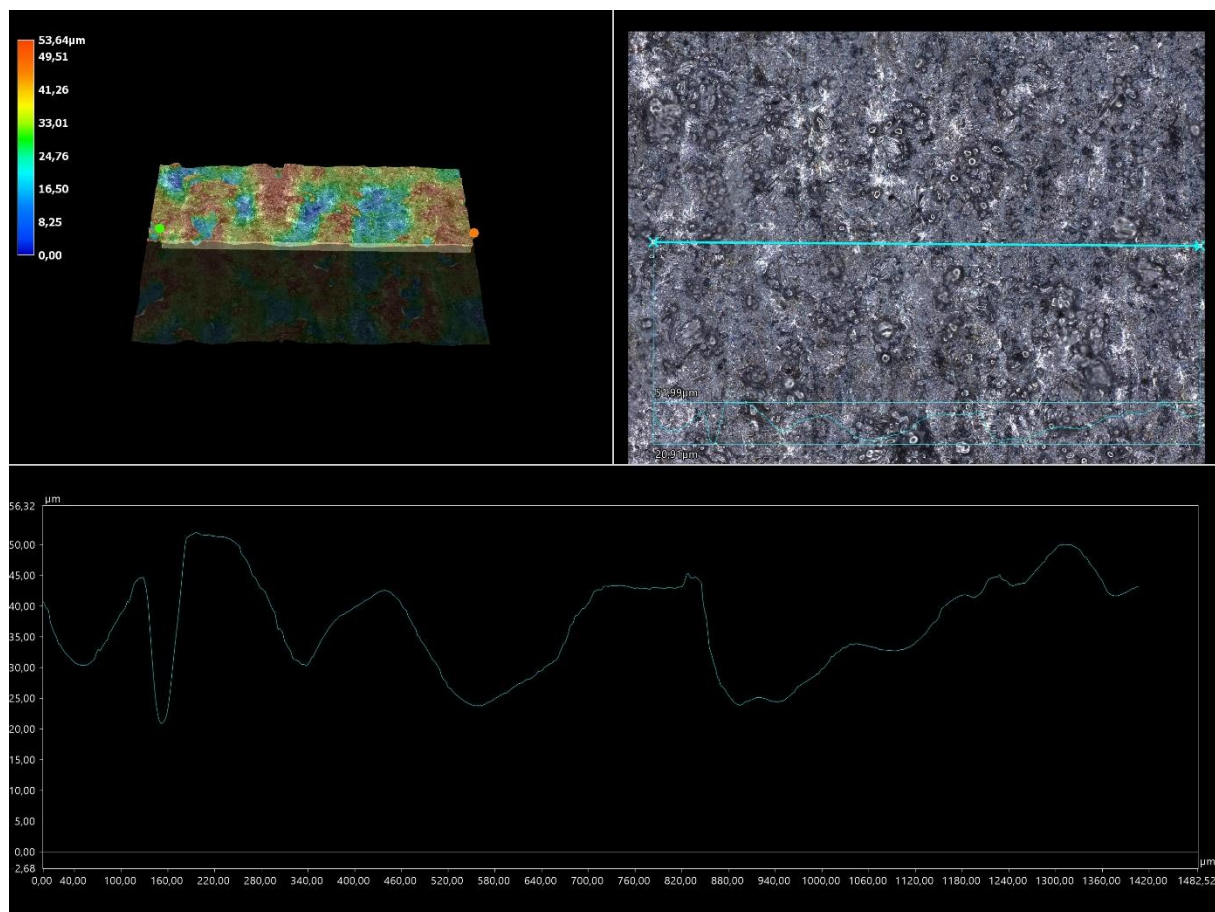


Figure S2 Example of line-profile extraction from digital microscopy data. The 3D height map (top left) and corresponding 2D microscopic image (top right) indicate the position of the extracted line profile. The height profile shown at the bottom was obtained along this line and used for the calculation of the arithmetic mean roughness R_a .

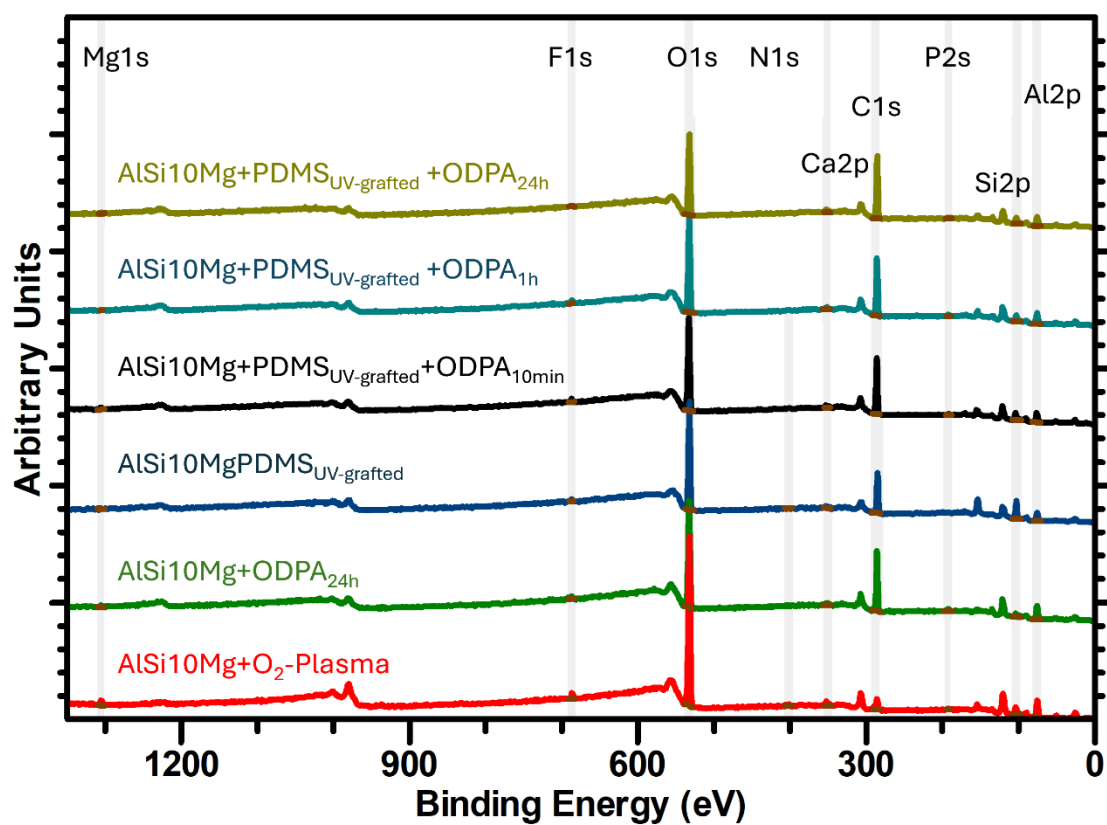


Figure S3. Representative XPS survey spectra used for the calculation of elemental composition shown in Table 5. Adapted from Ref. ¹¹⁵.

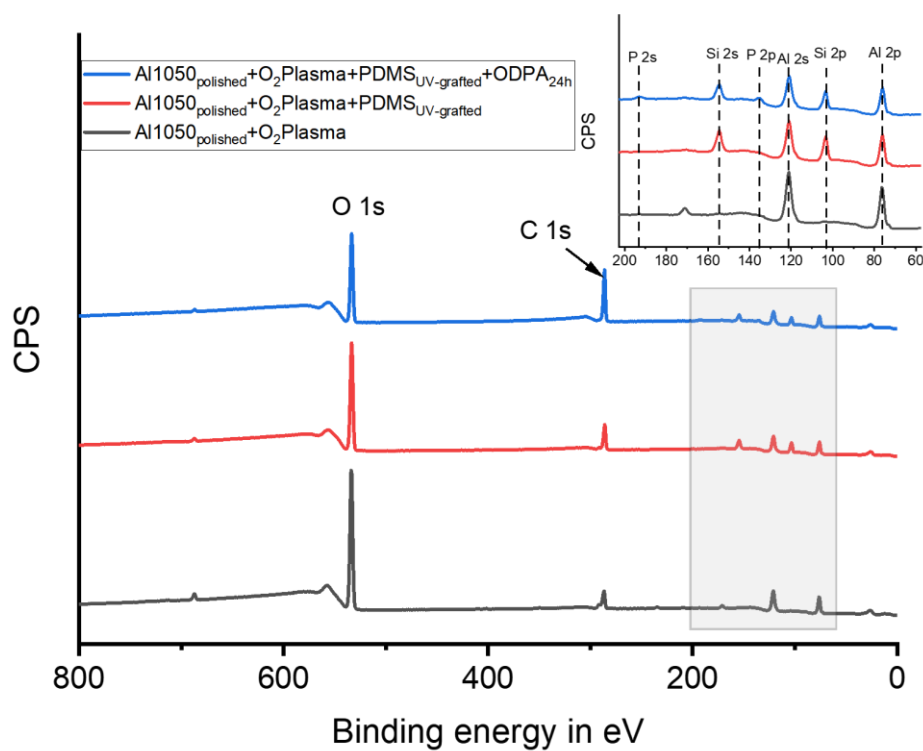


Figure S4. XPS survey spectra of (un-)modified polished Al1050 surfaces used for the calculation of elemental composition shown in Table 7. Reproduced from: Prüßner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", *Materials Chemistry and Physics*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ Minor changes were made.

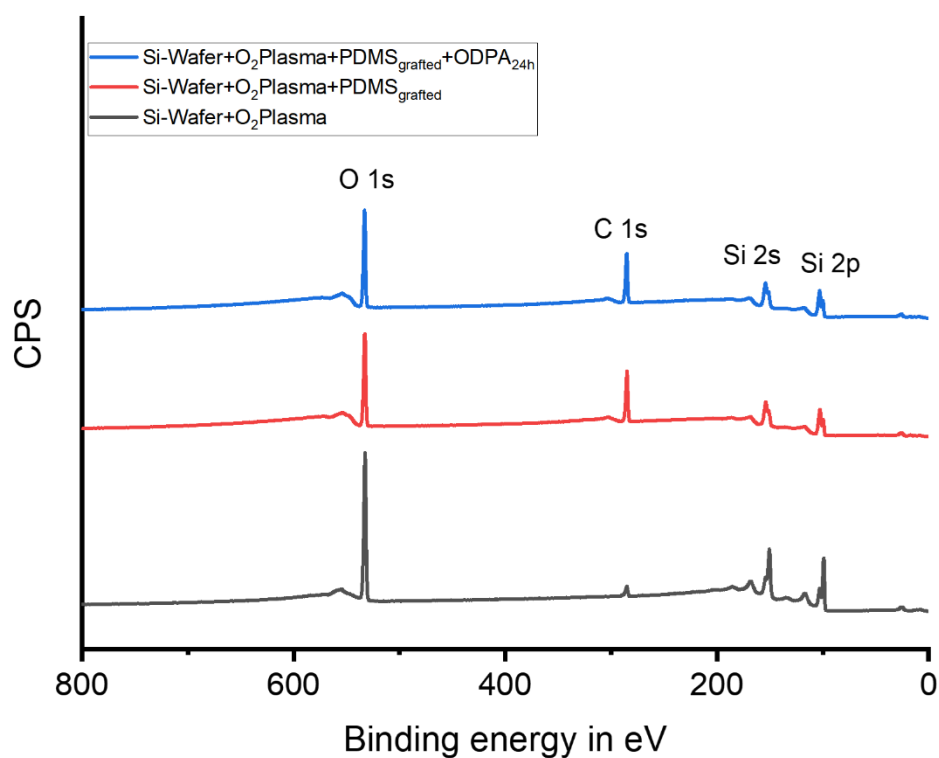


Figure S5. XPS survey spectra of (un-)modified Si-Wafer surfaces used for the calculation of elemental composition shown in Table 7. Reproduced from: Prüßner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", Materials Chemistry and Physics, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ No changes were made.

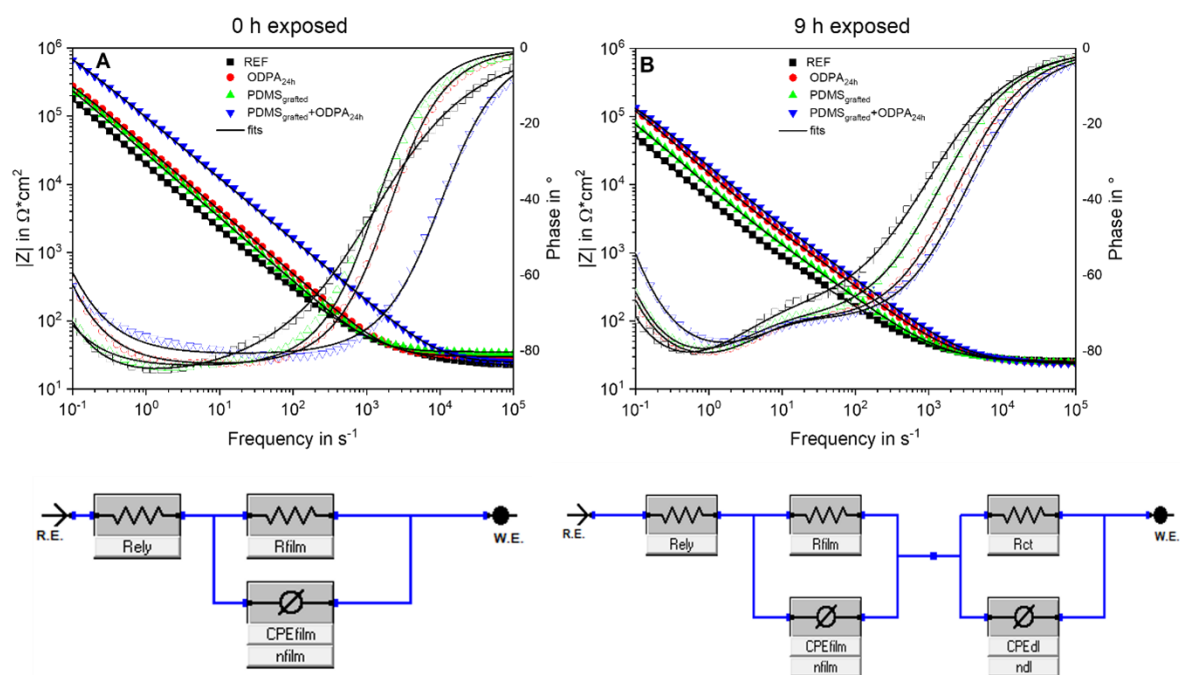


Figure S6. Equivalent circuit fitting results and the corresponding circuit diagrams of the electrochemical systems for as-built AlSi10Mg surfaces. The figure is divided into two columns representing the electrochemical systems used for fitting. (A) For short immersion intervals in 0.05 M NaCl solution ($t < 4$ h), the modified surfaces were fitted using a simplified circuit consisting of R_{ely} in series with a parallel $R_{film} || CPE_{film}$ element. This circuit describes a film-/oxide-dominated response, where the main impedance contribution is attributed to the thin organic film and native oxide layer. (B) For prolonged immersion ($t > 4$ h), the spectra were fitted using an extended circuit including an additional $R_{ct} || CPE_{dl}$ element, accounting for charge-transfer processes and double-layer formation after electrolyte penetration through the film/oxide interphase. For the unmodified Reference surface, the extended circuit shown in (B) was applied to all immersion intervals. Reproduced from: Prüßner et al. (2026) "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", Materials Chemistry and Physics, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ No changes were made except in the caption.

Table S1. XPS narrow scan fitting results for C 1s and Si 2p electrons from different surface modifications shown in Figure 31. The binding energy position of Si 2p electrons are given with respect to Si 2p 3/2 electrons. Reproduced from: Prüßner et al. (2026), "Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting", *Materials Chemistry and Physics*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹¹⁵ No changes were made.

Modification	Core level	Component	Binding energy in eV	FWHM	% of total area
Reference	Si 2p	Si metal	98.7	1.0	11.6
		Si oxide	103.3	1.9	88.4
	C 1s	C-C, C-H	285.8	1.7	64.9
		C-OH, C-O-C	287.3	1.7	16.9
		C=O	288.8	1.7	4.6
		O-C=O	290.1	1.7	13.7
ODPA	Si 2p	Si metal	98.7	1.0	19.8
		Si oxide	103.5	1.8	80.2
	C 1s	C-C, C-H	286.1	1.4	91.7
		C-OH, C-O-C	287.5	1.4	6.2
		C=O	289.1	1.4	0.4
		O-C=O	290.3	1.4	1.7
PDMS	Si 2p	Si metal	98.7	0.9	3.2
		Si oxide	103.2	1.7	24.4
		Si PDMS	102.8	1.2	72.4
	C 1s	C-C, C-H	286.3	1.4	27.0
		C-OH, C-O-C	287.8	1.4	2.4
		C=O	289.3	1.4	0.6
		O-C=O	290.5	1.4	2.0
		C-Si	285.3	1.3	68.0
PDMS+ODPA	Si 2p	Si metal	98.9	1.0	10.2
		Si oxide	103.7	1.9	41.5
		Si PDMS	103.0	1.3	48.3
	C 1s	C-C, C-H	285.9	1.5	88.2
		C-OH, C-O-C	287.4	1.5	2.8
		C=O	288.9	1.5	0.6
		O-C=O	290.2	1.5	0.9
		C-Si	285.6	0.9	7.5

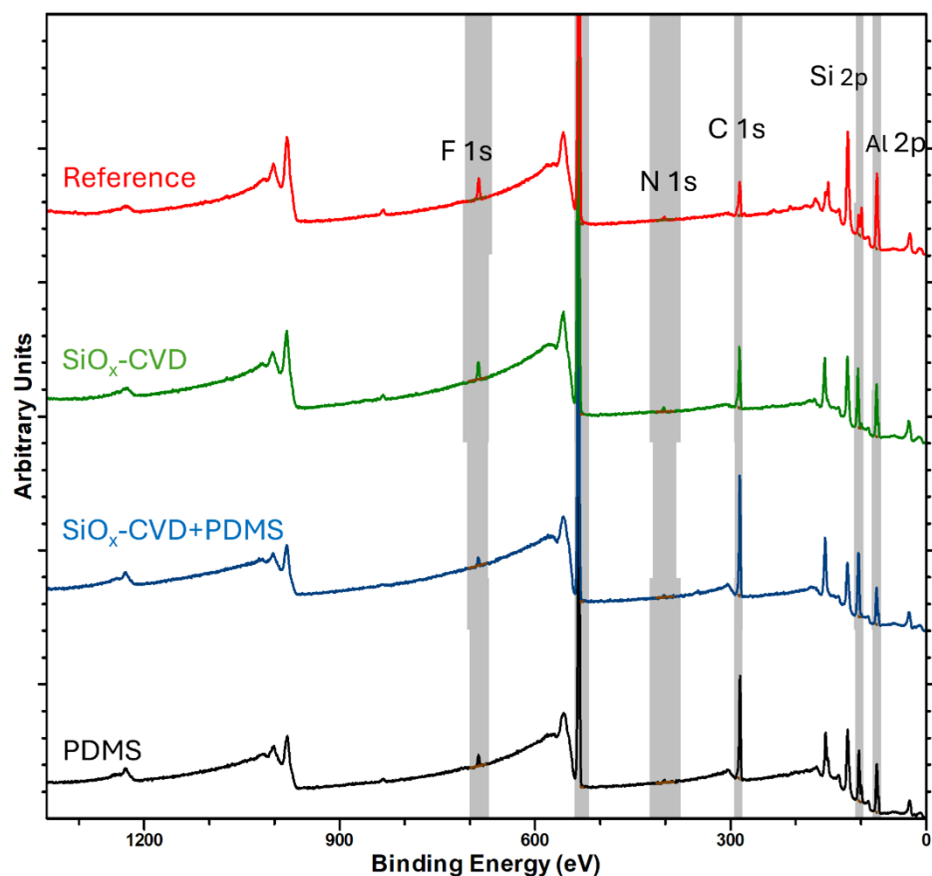


Figure S7. Representative XPS survey spectra of the investigated AM AlSi10Mg surface states. Spectra are shown for the polished and etched surface (Reference) and for modified (SiO_x-CVD, PDMS and SiO_x-CVD+PDMS) surfaces. Grey-shaded regions indicate the core-level ranges used for elemental quantification, while the corresponding background functions are shown in brown. The main photoelectron lines used for quantification are labeled. Further details on the XPS quantification procedure are provided in Section 3.5.5. Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, *Materials and Corrosion*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷² The wording of the caption has been adjusted.

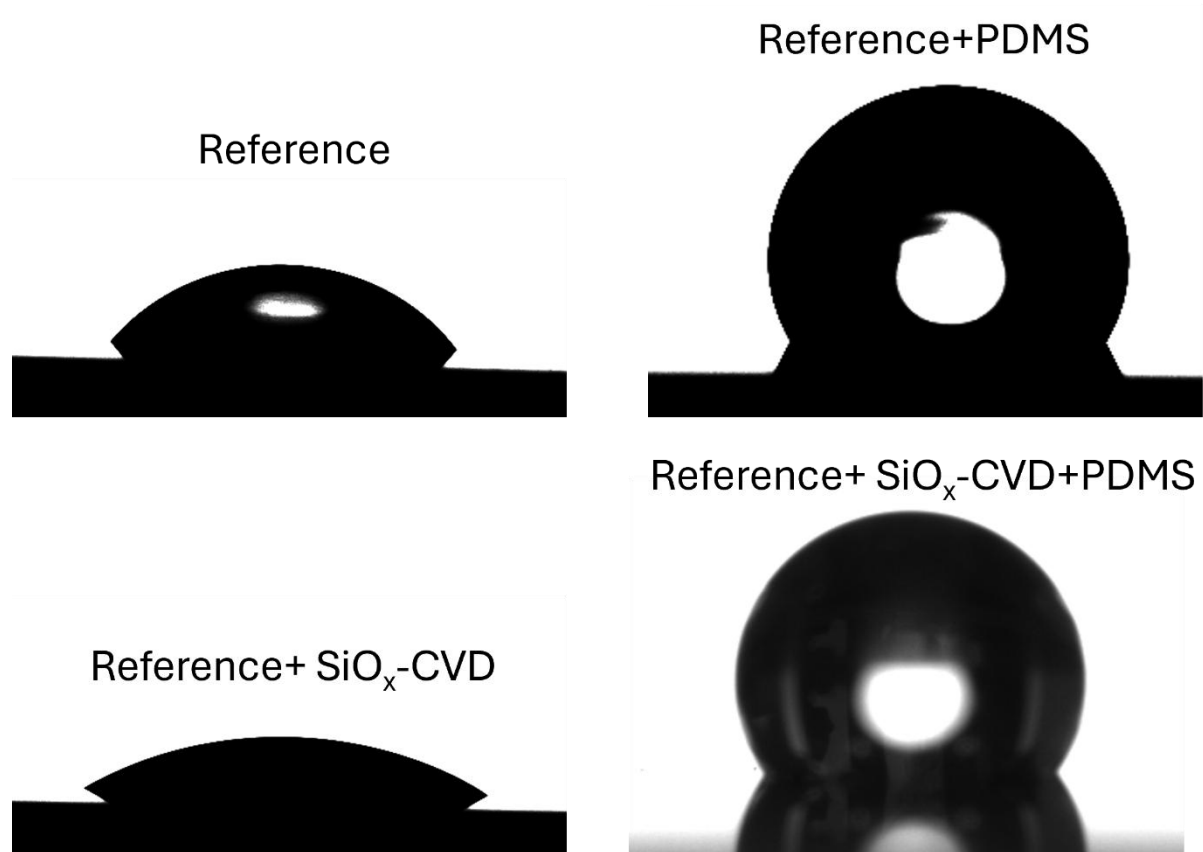


Figure S8. Representative water contact angle images of polished and etched AM AlSi10Mg surface states. The images show representative water droplets measured on the polished and etched Reference surface, the directly PDMS-modified surface, the SiO_x-CVD-modified surface, and the combined SiO_x-CVD+PDMS modification. The PDMS-containing surface states exhibit strongly increased water contact angles compared with the hydrophilic oxide-terminated Reference and SiO_x-CVD surfaces.

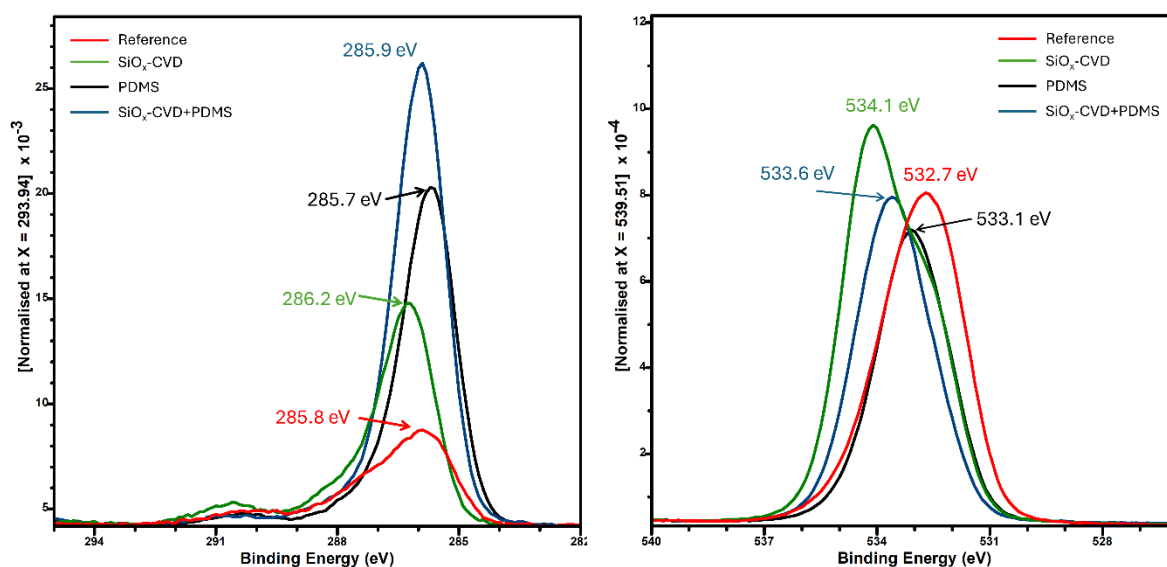


Figure S9. C1s (left image) and O1s (right image) XPS-spectra of the polished, etched and O₂-plasma treated AlSi10Mg surface (Reference, red line), Reference surface with applied SiO_x-CVD layer („SiO_x-CVD“, green line), Reference surface with PDMS layer („PDMS“, black line) and Reference surface with a combination of both modification layer („SiO_x-CVD +PDMS“, blue line). Additionally indicated are the respective binding energy peak positions. Reproduced from: Prübner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, *Materials and Corrosion*, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

Table S2. Details of the Si2p component fits shown in Figure 41 and Figure 43 of the main text. The GL(30) line shape represents a convolution of 70% Gaussian and 30% Lorentzian contributions. For the Si(0) component, this line shape was modified using an asymmetric function, $A(a,b,n)GL(30)$, where a and b define the asymmetry of the fit and n defines the width of the Gaussian used to convolute the basic peak shape.¹⁶⁷ A Shirley background was applied in all cases.¹⁶⁸ Reproduced from: Prüßner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

	Component	Si2p line	ID	Binding energy (BE) position	BE position C1s corrected (284.8 eV)	FWHM (eV)	Line Shape	Position constraints	FWHM constraints	Area constraints	Relative fraction of Si2p peak (%)
Reference (pristine)	Si(0)	3/2	A	98.8	No correction*	0.89	$A(0.45,0.3,100)GL(30)$	open	open	open	34.1
		1/2	B	99.4		0.89	$A(0.45,0.3,100)GL(30)$	$A + 0.6$	$A * 1$	$A * 0.5$	17.1
	Si oxide	3/2	C	103.1	102.1	1.77	GL(30)	open	open	open	32.6
		1/2	D	103.7	102.7	1.77	GL(30)	$C + 0.6$	$C * 1$	$C * 0.5$	16.3
SiO _x -CVD	Si(0)	3/2	A	99.0	No correction*	1.5	$A(0.45,0.3,100)GL(30)$	open	open	open	5.1
		1/2	B	99.6		1.5	$A(0.45,0.3,100)GL(30)$	$A + 0.6$	$A * 1$	$A * 0.5$	2.6
	Si oxide	3/2	C	103.2	No information†	1.6	GL(30)	open	open	open	11.2
		1/2	D	103.8		1.6	GL(30)	$C + 0.6$	$C * 1$	$C * 0.5$	5.6
	Si CVD	1/2	E	104.7	103.3	1.5	GL(30)	open	open	open	50.3
		3/2	F	105.3	103.9	1.5	GL(30)	$E + 0.6$	$E * 1$	$E * 0.5$	25.2
PDMS	Si(0)	3/2	A	99.0	No correction*	1.02	$A(0.45,0.3,100)GL(30)$	open	open	open	14.5
		1/2	B	99.6		1.02	$A(0.45,0.3,100)GL(30)$	$A + 0.6$	$A * 1$	$A * 0.5$	7.3
	Si oxide/PDMS	3/2	C	103.1	Add. C 1s	1.57	GL(30)	open	open	open	52.2
		1/2	D	103.7	component‡	1.57	GL(30)	$C + 0.6$	$C * 1$	$C * 0.5$	26.1
SiO _x -CVD +PDMS	Si(0)	3/2	A	99.1	No correction*	1.59	$A(0.45,0.3,100)GL(30)$	open	open	open	2.6
		1/2	B	99.7		1.59	$A(0.45,0.3,100)GL(30)$	$A + 0.6$	$A * 1$	$A * 0.5$	1.3
	Si oxide/PDMS	3/2	C	103.2	Add. C 1s component‡	1.26	GL(30)	open	open	open	33.0
		1/2	D	103.8		1.26	GL(30)	$C + 0.6$	$C * 1$	$C * 0.5$	16.5
	Si CVD	3/2	E	104.4	No information†	1.7	GL(30)	open	open	open	31.1
		1/2	F	105.0		1.7	GL(30)	$E + 0.6$	$E * 1$	$E * 0.5$	15.5

*No charging-induced shift of the metallic bulk component is expected; thus, no C 1s referencing was applied

†C1s referencing was not applied, as the C1s signal is not directly associated with this species.

‡C 1s referencing was not applied to this component, as the C 1s signal originates from an additional C–Si species.

Table S3. Details of the Al2p component fits shown in Figure 41 and Figure 43 of the main text. The GL(30) line shape represents a convolution of 70% Gaussian and 30% Lorentzian contributions. For the Si(0) component, this line shape was modified using an asymmetric function, $A(a,b,n)GL(30)$, where a and b define the asymmetry of the fit and n defines the width of the Gaussian used to convolute the basic peak shape.¹⁶⁷ A Shirley background was applied in all cases.¹⁶⁸ Reproduced from: Pr  bner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ The wording of the caption has been adjusted.

	Component	Al2p line	ID	Binding energy (BE) position	BE position C 1s corrected (284.8 eV)	FWHM (eV)	Line Shape	Position constraint	FWHM constraint	Area constraint	Relative fraction of Al2p peak (%)
Reference (pristine)	Al(0)	3/2	A	72.5	No correction*	0.52	A(0.4,0.9,100)GL(30)	open	open	open	7.5
		1/2	B	72.9		0.52	A(0.4,0.9,100)GL(30)	A + 0.4	A * 1	A * 0.5	3.7
	Al oxide	3/2	C	75.3	74.3	1.51	GL(30)	open	open	open	39.0
		1/2	D	75.7	74.7	1.51	GL(30)	C + 0.4	C * 1	C * 0.5	19.5
	Al oxide/hydroxide	3/2	E	76.2	75.2	2.14	GL(30)	open	open	open	20.2
		1/2	F	76.6	75.6	2.14	GL(30)	E + 0.4	E * 1	E * 0.5	10.1
SiO _x -CVD	Al(0)	3/2	A	72.6	No correction*	0.5	A(0.4,0.9,100)GL(30)	open	open	open	7.6
		1/2	B	73.1		0.5	A(0.4,0.9,100)GL(30)	A + 0.4	A * 1	A * 0.5	3.8
	Al oxide	3/2	C	75.8	No information†	1.64	GL(30)	open	open	open	59.1
		1/2	D	76.2		1.64	GL(30)	C + 0.4	C * 1	C * 0.5	29.5
PDMS	Al(0)	3/2	A	72.5	No correction*	0.5	A(0.4,0.9,100)GL(30)	open	open	open	9.7
		1/2	B	72.9		0.5	A(0.4,0.9,100)GL(30)	A + 0.4	A * 1	A * 0.5	4.8
	Al oxide	3/2	C	75.7	No information†	1.7	GL(30)	open	open	open	57.0
		1/2	D	76.1		1.7	GL(30)	C + 0.4	C * 1	C * 0.5	28.5
SiO _x -CVD +PDMS	Al(0)	3/2	A	72.6	No correction*	0.5	A(0.4,0.9,100)GL(30)	open	open	open	8.4
		1/2	B	73.1		0.5	A(0.4,0.9,100)GL(30)	A + 0.4	A * 1	A * 0.5	4.2
	Al oxide	3/2	C	75.9	No information†	1.6	GL(30)	open	open	open	58.3
		1/2	D	76.3		1.6	GL(30)	C + 0.4	C * 1	C * 0.5	29.1
*No charging-induced shift of the metallic bulk component is expected; thus, no C 1s referencing was applied											
†C1s referencing was not applied, as the C1s signal is not directly associated with this species.											

Table S4. TPP-2M input parameters and calculated IMFPs for Si photoelectrons in kyanite (Al_2SiO_5) and PDMS. Reproduced from: Průbner et al. (2026), „Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting“, Materials and Corrosion, CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>.¹⁷⁰ No changes were made.

Material	$\Delta E_{\text{Bandgap}}^*$ [eV]	Valence electrons	Density [g/cm ³]	$\lambda_{\text{TPP-2M}}^*$ [nm]
Al_2SiO_4	9.1	40	3.61	3.6
PDMS	≈ 5.5	24	0.97	3.9

*Ref.^{203,204}

*Ref.^{192,205}

Table S5. Element quantification based on XP survey spectra. Affinity of ODPA molecules towards single PDMS and combined SiO_x-CVD+PDMS modification on polished and etched AM AlSi10Mg surfaces.

Core level	PDMS	PDMS+ ODPA _{24h}	SiO _x - CVD+PDMS	SiO _x - CVD+PDMS+ ODPA _{24h}
O1s	40.4	28.8	34.2	29.2
C1s	19.3	39.3	29.4	38.8
Al2p	27.3	20.9	12.8	9.7
Si2p	12.9	9.4	23.2	21.5
P2s	-	1.0	-	0.6
F1s	0.1	0.4	0.3	0.1
N1s	-	0.2	0.2	0.2

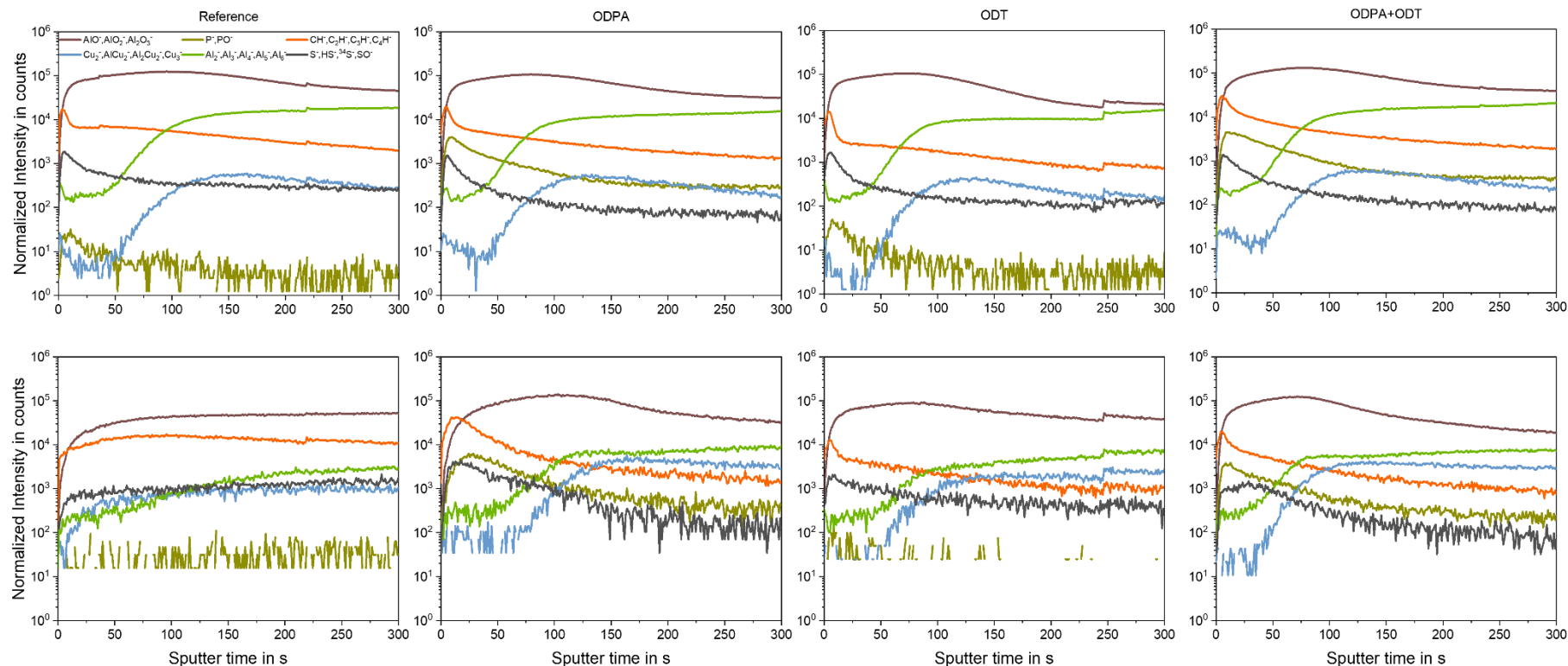


Figure S10. ToF-SIMS sputter-depth profiles of the investigated AlCu5.9 model-alloy surface states. Profiles are shown for Reference, ODPA, ODT, and ODPA+ODT surfaces over a sputter-time range of 0–300 s. The upper panels correspond to the Al-rich matrix ROIs, and the lower panels correspond to the Cu-rich intermetallic ROIs, operationally referred to as Al₂Cu regions. The displayed secondary ion groups comprise sulfur-containing species (S⁻, HS⁻, ³⁴S⁻, SO⁻), phosphorus-containing species (P⁻, PO⁻), hydrocarbon fragments (CH⁻, C₂H⁻, C₃H⁻, C₄H⁻), Al-related bulk fragments (Al₂⁻, Al₃⁻, Al₄⁻, Al₅⁻, Al₆⁻), Cu-rich intermetallic-region-related fragments (Cu₂⁻, AlCu₂⁻, Al₂Cu₂⁻, Cu₃⁻), and aluminum oxide-related fragments (AlO⁻, AlO₂⁻, Al₂O₃⁻). All intensities are shown as normalized secondary ion intensities. The normalization factors are specified in Section 3.5.6. The profiles provide the basis for selecting the surface-near and phase-identifying sputter intervals used in the ToF-SIMS analysis.

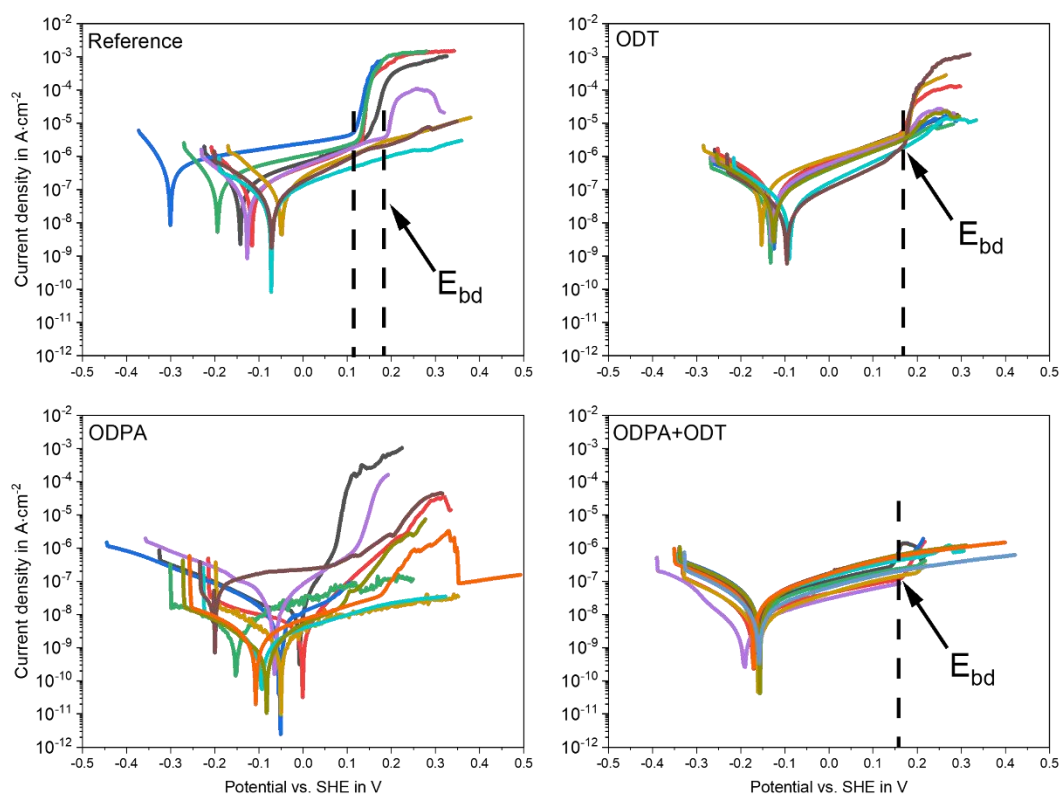


Figure S11. Individual LSV curves of untreated and molecularly treated AW2024 surfaces recorded in chloride-free 0.1 M Na_2SO_4 electrolyte. The figure shows all LSV measurements obtained for the Reference, ODPA, ODT, and ODPA+ODT surface states. The curves were recorded after EIS characterization and were used for the Tafel evaluation summarized in Table 19. The marked E_{bd} regions indicate the approximate potential ranges in which a pronounced anodic current increase occurs and are interpreted as breakdown-related onset regions of the passive film under the applied measurement conditions.

8. References

- (1) Zhou, K.; Liu, T.; Zhou, L. Industry 4.0: Towards future industrial opportunities and challenges. In *2015 12th International Conference on Fuzzy Systems and Knowledge Discovery (FSKD)*; IEEE, 2015; pp 2147–2152. DOI: 10.1109/FSKD.2015.7382284.
- (2) Bonilla, S. H.; Silva, H. R. O.; Da Terra Silva, M.; Franco Gonçalves, R.; Sacomano, J. B. Industry 4.0 and Sustainability Implications: A Scenario-Based Analysis of the Impacts and Challenges. *Sustainability* **2018**, *10* (10), 3740. DOI: 10.3390/su10103740.
- (3) Oláh, J.; Aburumman, N.; Popp, J.; Khan, M. A.; Haddad, H.; Kitukutha, N. Impact of Industry 4.0 on Environmental Sustainability. *Sustainability* **2020**, *12* (11), 4674. DOI: 10.3390/su12114674.
- (4) Koch, G. 1 - Cost of corrosion. In *Trends in oil and gas corrosion research and technologies: Production and transmission*; Sherik, A. M., Ed.; Woodhead Publishing series in energy; WP Woodhead Publishing an imprint of Elsevier, 2017; pp 3–30. DOI: 10.1016/B978-0-08-101105-8.00001-2.
- (5) Al-Alimi, S.; Yusuf, N. K.; Ghaleb, A. M.; Lajis, M. A.; Shamsudin, S.; Zhou, W.; Altharan, Y. M.; Abdulwahab, H. S.; Saif, Y.; Didane, D. H.; S T T, I.; Adam, A. Recycling aluminium for sustainable development: A review of different processing technologies in green manufacturing. *Results in Engineering* **2024**, *23*, 102566. DOI: 10.1016/j.rineng.2024.102566.
- (6) Emadi, P.; Andilab, B.; Ravindran, C. Engineering Lightweight Aluminum and Magnesium Alloys for a Sustainable Future. *J Indian Inst Sci* **2022**, *102* (1), 405–420. DOI: 10.1007/s41745-021-00267-9.
- (7) Sun, Y. The use of aluminum alloys in structures: Review and outlook. *Structures* **2023**, *57*, 105290. DOI: 10.1016/j.istruc.2023.105290.
- (8) You, X.; Xing, Z.; Jiang, S.; Zhu, Y.; Lin, Y.; Qiu, H.; Nie, R.; Yang, J.; Hui, D.; Chen, W.; Chen, Y. A review of research on aluminum alloy materials in structural engineering. *Developments in the Built Environment* **2024**, *17*, 100319. DOI: 10.1016/j.dibe.2023.100319.
- (9) Tisza, M.; Lukács, Z. High strength aluminum alloys in car manufacturing. *IOP Conf. Ser.: Mater. Sci. Eng.* **2018**, *418*, 12033. DOI: 10.1088/1757-899X/418/1/012033.
- (10) Stojanovic, B.; Bukvic, M.; Epler, I. Application of Aluminum and Aluminum Alloys in Engineering. *Applied Engineering Letters* **2018**, *3* (2), 52–62. DOI: 10.18485/aeletters.2018.3.2.2.
- (11) Li, J.; Dang, J. A Summary of Corrosion Properties of Al-Rich Solid Solution and Secondary Phase Particles in Al Alloys. *Metals* **2017**, *7* (3), 84. DOI: 10.3390/met7030084.
- (12) Czaban, M. Aircraft Corrosion – Review of Corrosion Processes and its Effects in Selected Cases. *Fatigue of Aircraft Structures* **2018**, *2018* (10), 5–20. DOI: 10.2478/fas-2018-0001.
- (13) Sinyavskii, V. S.; v. d. Kalinin. Marine Corrosion and Protection of Aluminum Alloys According to Their Composition and Structure. *Prot Met* **2005**, *41* (4), 317–328. DOI: 10.1007/s11124-005-0046-8.
- (14) Staley, J. T. Corrosion of Aluminium Aerospace Alloys. *MSF* **2016**, *877*, 485–491. DOI: 10.4028/www.scientific.net/MSF.877.485.
- (15) Ahmad, Z. *Recent Trends in Processing and Degradation of Aluminium Alloys*; InTech, 2011. DOI: 10.5772/741.
- (16) Lehmhus, D.; Busse, M.; Herrmann, A. S.; Kayvantash, K. *Structural Materials and Processes in Transportation*; Wiley, 2013. DOI: 10.1002/9783527649846.
- (17) Frazier, W. E. Metal Additive Manufacturing: A Review. *J. of Materi Eng and Perform* **2014**, *23* (6), 1917–1928. DOI: 10.1007/s11665-014-0958-z.

- (18) Trevisan, F.; Calignano, F.; Lorusso, M.; Pakkanen, J.; Aversa, A.; Ambrosio, E. P.; Lombardi, M.; Fino, P.; Manfredi, D. On the Selective Laser Melting (SLM) of the AlSi10Mg Alloy: Process, Microstructure, and Mechanical Properties. *Materials (Basel, Switzerland)* **2017**, *10* (1). DOI: 10.3390/ma10010076.
- (19) Kusoglu, I. M.; Vieth, P.; Heiland, S.; Huber, F.; Lüddecke, A.; Ziefuss, A. R.; Kwade, A.; Schmidt, M.; Schaper, M.; Barcikowski, S.; Grundmeier, G. Microstructure and corrosion properties of PBF-LB produced carbide nanoparticles additivated AlSi10Mg parts. *Procedia CIRP* **2022**, *111*, 10–13. DOI: 10.1016/j.procir.2022.08.046.
- (20) Dilberoglu, U. M.; Gharehpapagh, B.; Yaman, U.; Dolen, M. The Role of Additive Manufacturing in the Era of Industry 4.0. *Procedia Manufacturing* **2017**, *11*, 545–554. DOI: 10.1016/j.promfg.2017.07.148.
- (21) Gatto, A.; Cappelletti, C.; Defanti, S.; Fabbri, F. The Corrosion Behaviour of Additively Manufactured AlSi10Mg Parts Compared to Traditional Al Alloys. *Metals* **2023**, *13* (5), 913. DOI: 10.3390/met13050913.
- (22) Sousa Araujo, J. V. de; Costa, I.; Zhou, X. Comparison of Constituent Intermetallic Particles in Different Aluminium Alloys. *Metallogr. Microstruct. Anal.* **2025**, *14* (1), 106–119. DOI: 10.1007/s13632-025-01170-w.
- (23) Birbilis, N.; Buchheit, R. G. Electrochemical Characteristics of Intermetallic Phases in Aluminum Alloys. *J. Electrochem. Soc.* **2005**, *152* (4), B140. DOI: 10.1149/1.1869984.
- (24) Jin, Y.; Liu, M.; Zhang, C.; Leygraf, C.; Wen, L.; Pan, J. First-Principle Calculation of Volta Potential of Intermetallic Particles in Aluminum Alloys and Practical Implications. *J. Electrochem. Soc.* **2017**, *164* (9), C465–C473. DOI: 10.1149/2.0191709jes.
- (25) Marola, S.; Bosia, S.; Veltro, A.; Fiore, G.; Manfredi, D.; Lombardi, M.; Amato, G.; Baricco, M.; Battezzati, L. Residual stresses in additively manufactured AlSi10Mg: Raman spectroscopy and X-ray diffraction analysis. *Materials & Design* **2021**, *202*, 109550. DOI: 10.1016/j.matdes.2021.109550.
- (26) Davoodi, A.; Pan, J.; Leygraf, C.; Norgren, S. The Role of Intermetallic Particles in Localized Corrosion of an Aluminum Alloy Studied by SKPFM and Integrated AFM/SECM. *J. Electrochem. Soc.* **2008**, *155* (5), C211. DOI: 10.1149/1.2883737.
- (27) Zhu, Y.; Sun, K.; Frankel, G. S. Intermetallic Phases in Aluminum Alloys and Their Roles in Localized Corrosion. *J. Electrochem. Soc.* **2018**, *165* (11), C807–C820. DOI: 10.1149/2.0931811jes.
- (28) Berlanga-Labari, C.; Biezma-Moraleda, M. V.; Rivero, P. J. Corrosion of Cast Aluminum Alloys: A Review. *Metals* **2020**, *10* (10), 1384. DOI: 10.3390/met10101384.
- (29) Becker, M. Chromate-free chemical conversion coatings for aluminum alloys. *Corrosion Reviews* **2019**, *37* (4), 321–342. DOI: 10.1515/corrrev-2019-0032.
- (30) Bethencourt, M.; Botana, F. J.; Cano, M. J.; Marcos, M. Advanced generation of green conversion coatings for aluminium alloys. *Applied Surface Science* **2004**, *238* (1–4), 278–281. DOI: 10.1016/j.apsusc.2004.05.268.
- (31) Harvey, T. G. Cerium-based conversion coatings on aluminium alloys: a process review. *Corrosion Engineering, Science and Technology* **2013**, *48* (4), 248–269. DOI: 10.1179/1743278213Y.0000000089.
- (32) Araujo, J. V. d. S.; Milagre, M.; Costa, I. A historical, statistical and electrochemical approach on the effect of microstructure in the anodizing of Al alloys: a review. *Critical Reviews in Solid State and Materials Sciences* **2024**, *49* (4), 521–581. DOI: 10.1080/10408436.2023.2230250.

- (33) Paz Martínez-Viademonte, M.; Abrahami, S. T.; Hack, T.; Burchardt, M.; Terryn, H. A Review on Anodizing of Aerospace Aluminum Alloys for Corrosion Protection. *Coatings* **2020**, *10* (11), 1106. DOI: 10.3390/coatings10111106.
- (34) Chhipa, S. M.; Sharma, S.; Kumar Bagha, A. Recent development in polymer coating to prevent corrosion in metals: A review. *Materials Today: Proceedings* **2024**. DOI: 10.1016/j.matpr.2024.09.001.
- (35) Telegdi, J. Formation of Self-Assembled Anticorrosion Films on Different Metals. *Materials (Basel, Switzerland)* **2020**, *13* (22). DOI: 10.3390/ma13225089.
- (36) Kühnle, A. Self-assembly of organic molecules at metal surfaces. *Current Opinion in Colloid & Interface Science* **2009**, *14* (2), 157–168. DOI: 10.1016/j.cocis.2008.01.001.
- (37) Otero, R.; Gallego, J. M.; Parga, A. L. V. de; Martín, N.; Miranda, R. Molecular self-assembly at solid surfaces. *Advanced materials (Deerfield Beach, Fla.)* **2011**, *23* (44), 5148–5176. DOI: 10.1002/adma.201102022.
- (38) Schwartz, D. K. Mechanisms and kinetics of self-assembled monolayer formation. *Annual review of physical chemistry* **2001**, *52*, 107–137. DOI: 10.1146/annurev.physchem.52.1.107.
- (39) Whitesides, G. M.; Kriebel, J. K.; Love, J. C. Molecular engineering of surfaces using self-assembled monolayers. *Science progress* **2005**, *88* (Pt 1), 17–48. DOI: 10.3184/003685005783238462.
- (40) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chemical reviews* **1996**, *96* (4), 1533–1554. DOI: 10.1021/cr9502357.
- (41) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chemical reviews* **2005**, *105* (4), 1103–1169. DOI: 10.1021/cr0300789.
- (42) Zhao, R. Three Stages of Phosphonic Acid Modification Applied to the Aluminum Oxide Surface, ETH Zurich, 2022. DOI: 10.3929/ethz-b-000588241. DOI: 10.3929/ethz-b-000588241.
- (43) Zhao, R.; Rupper, P.; Gaan, S. Recent Development in Phosphonic Acid-Based Organic Coatings on Aluminum. *Coatings* **2017**, *7* (9), 133. DOI: 10.3390/coatings7090133.
- (44) Teisala, H.; Baumli, P.; Weber, S. A. L.; Vollmer, D.; Butt, H.-J. Grafting Silicone at Room Temperature—a Transparent, Scratch-resistant Nonstick Molecular Coating. *Langmuir : the ACS journal of surfaces and colloids* **2020**, *36* (16), 4416–4431. DOI: 10.1021/acs.langmuir.9b03223.
- (45) Krumpfer, J. W.; McCarthy, T. J. Rediscovering silicones: "unreactive" silicones react with inorganic surfaces. *Langmuir : the ACS journal of surfaces and colloids* **2011**, *27* (18), 11514–11519. DOI: 10.1021/la202583w.
- (46) Tesler, A. B.; Prado, L. H.; Khusniyarov, M. M.; Thievessen, I.; Mazare, A.; Fischer, L.; Virtanen, S.; Goldmann, W. H.; Schmuki, P. A One-Pot Universal Approach to Fabricate Lubricant-Infused Slippery Surfaces on Solid Substrates. *Adv. Funct. Mater.* **2021**, *31* (27), 2101090. DOI: 10.1002/adfm.202101090.
- (47) Schindelholz, E.; Kelly, R. G. Wetting phenomena and time of wetness in atmospheric corrosion: a review. *Corrosion Reviews* **2012**, *30* (5-6), 135–170. DOI: 10.1515/correv-2012-0015.
- (48) McCafferty, E. *Introduction to Corrosion Science*; Springer New York, 2010. DOI: 10.1007/978-1-4419-0455-3.
- (49) Revie, R. W.; Uhlig, H. H. *Corrosion and Corrosion Control*; Wiley, 2008. DOI: 10.1002/9780470277270.
- (50) Vargel, C.; Germain, J.-M. *Corrosion of aluminium*, Second edition; Elsevier Science, 2020. ISBN: 978-0-08-099925-8.

- (51) Deltombe, E.; Pourbaix, M. The Electrochemical Behavior of Aluminum: Potential pH Diagram of the System Al-H₂O at 25 C. *CORROSION* **1958**, *14* (11), 16–20. DOI: 10.5006/0010-9312-14.11.16.
- (52) Wagner, C.; Traud, W. Über die Deutung von Korrosionsvorgängen durch Überlagerung von elektrochemischen Teilvorgängen und über die Potentialbildung an Mischelektroden. *Zeitschrift für Elektrochemie und angewandte physikalische Chemie* **1938**, *44* (7), 391–402. DOI: 10.1002/bbpc.19380440702.
- (53) Cho, S.; Weitzner, S. E.; Zagalskaya, A.; Hsu, T.; Pham, T. A.; Castaneda, H.; Wood, B. C.; Orme, C. A. Revisiting a minimally destructive analytic approach for determining electrochemical kinetic parameters: Measuring aluminum corrosion across a wide pH range based on the Butler-Volmer equation. *Corrosion Science* **2025**, *251*, 112900. DOI: 10.1016/j.corsci.2025.112900.
- (54) Rautio, T.; Torbati-Sarraf, H.; Allam, T.; Järvenpää, A.; Hamada, A. Enhancement of electrical conductivity and corrosion resistance by gold-nickel coating of additively manufactured AlSi10Mg alloy. *Journal of Materials Research and Technology* **2022**, *17*, 521–536. DOI: 10.1016/j.jmrt.2022.01.022.
- (55) Sato, N. An overview on the passivity of metals. *Corrosion Science* **1990**, *31*, 1–19. DOI: 10.1016/0010-938X(90)90086-K.
- (56) Frankel, G. S.; Sridhar, N. Understanding localized corrosion. *Materials Today* **2008**, *11* (10), 38–44. DOI: 10.1016/S1369-7021(08)70206-2.
- (57) Ikeuba, A. I.; Njoku, C. N.; Ekerenam, O. O.; Njoku, D. I.; Udoh, I. I.; Daniel, E. F.; Uzoma, P. C.; Etim, I.-I. N.; Okonkwo, B. O. A review of the electrochemical and galvanic corrosion behavior of important intermetallic compounds in the context of aluminum alloys. *RSC advances* **2024**, *14* (43), 31921–31953. DOI: 10.1039/D4RA06070A.
- (58) Cornette, P.; Zanna, S.; Seyeux, A.; Costa, D.; Marcus, P. The native oxide film on a model aluminium-copper alloy studied by XPS and ToF-SIMS. *Corrosion Science* **2020**, *174*, 108837. DOI: 10.1016/j.corsci.2020.108837.
- (59) McCafferty, E. Sequence of steps in the pitting of aluminum by chloride ions. *Corrosion Science* **2003**, *45* (7), 1421–1438. DOI: 10.1016/S0010-938X(02)00231-7.
- (60) Akpanyung, K.; Loto, R. Pitting corrosion evaluation: a review. *J. Phys.: Conf. Ser.* **2019**, *1378* (2), 22088. DOI: 10.1088/1742-6596/1378/2/022088.
- (61) Szklarska-Smialowska, Z. Pitting corrosion of aluminum. *Corrosion Science* **1999**, *41* (9), 1743–1767. DOI: 10.1016/S0010-938X(99)00012-8.
- (62) McCafferty, E.; Wightman, J. P. Determination of the Surface Isoelectric Point of Oxide Films on Metals by Contact Angle Titration. *Journal of Colloid and Interface Science* **1997**, *194* (2), 344–355. DOI: 10.1006/jcis.1997.5138.
- (63) Natishan, P. M.; O'Grady, W. E. Chloride Ion Interactions with Oxide-Covered Aluminum Leading to Pitting Corrosion: A Review. *J. Electrochem. Soc.* **2014**, *161* (9), C421–C432. DOI: 10.1149/2.1011409jes.
- (64) Blücher, D. B.; Svensson, J.-E.; Johansson, L.-G. The influence of CO₂, AlCl₃·6H₂O, MgCl₂·6H₂O, Na₂SO₄ and NaCl on the atmospheric corrosion of aluminum. *Corrosion Science* **2006**, *48* (7), 1848–1866. DOI: 10.1016/j.corsci.2005.05.027.
- (65) LeBozec, N.; Thierry, D.; Persson, D.; Stoullil, J. Atmospheric Corrosion of Zinc-Aluminum Alloyed Coated Steel in Depleted Carbon Dioxide Environments. *J. Electrochem. Soc.* **2018**, *165* (7), C343–C353. DOI: 10.1149/2.0721807jes.
- (66) Cheng, Y. L.; Zhang, Z.; Cao, F. H.; Li, J. F.; Zhang, J. Q.; Wang, J. M.; Cao, C. N. A study of the corrosion of aluminum alloy 2024-T3 under thin electrolyte layers. *Corrosion Science* **2004**, *46* (7), 1649–1667. DOI: 10.1016/j.corsci.2003.10.005.

- (67) Cruz, R.; Nishikata, A.; Tsuru, T. Pitting corrosion mechanism of stainless steels under wet-dry exposure in chloride-containing environments. *Corrosion Science* **1998**, *40* (1), 125–139. DOI: 10.1016/S0010-938X(97)00124-8.
- (68) Sereda, P. J. Atmospheric corrosion of metals. *Canadian Building Digest, CBD-170*. DOI: 10.4224/40000782.
- (69) Cai, Y.; Xu, Y.; Zhao, Y.; Ma, X. Atmospheric corrosion prediction: a review. *Corrosion Reviews* **2020**, *38* (4), 299–321. DOI: 10.1515/corrrev-2019-0100.
- (70) Peng, C.; Chen, L.; Tang, M. A database for deliquescence and efflorescence relative humidities of compounds with atmospheric relevance. *Fundamental research* **2022**, *2* (4), 578–587. DOI: 10.1016/j.fmre.2021.11.021.
- (71) Koushik, B. G.; van den Steen, N.; Mamme, M. H.; van Ingelgem, Y.; Terryn, H. Review on modelling of corrosion under droplet electrolyte for predicting atmospheric corrosion rate. *Journal of Materials Science & Technology* **2021**, *62*, 254–267. DOI: 10.1016/j.jmst.2020.04.061.
- (72) Liao, X.; Cao, F.; Zheng, L.; Liu, W.; Chen, A.; Zhang, J.; Cao, C. Corrosion behaviour of copper under chloride-containing thin electrolyte layer. *Corrosion Science* **2011**, *53* (10), 3289–3298. DOI: 10.1016/j.corsci.2011.06.004.
- (73) Zhong, X.; Zhang, G.; Qiu, Y.; Chen, Z.; Guo, X.; Fu, C. The corrosion of tin under thin electrolyte layers containing chloride. *Corrosion Science* **2013**, *66*, 14–25. DOI: 10.1016/j.corsci.2012.08.040.
- (74) Tsutsumi, Y.; Nishikata, A.; Tsuru, T. Pitting corrosion mechanism of Type 304 stainless steel under a droplet of chloride solutions. *Corrosion Science* **2007**, *49* (3), 1394–1407. DOI: 10.1016/j.corsci.2006.08.016.
- (75) Chen, C.; Mansfeld, F. Potential distribution in the evans drop experiment. *Corrosion Science* **1997**, *39* (2), 409–413. DOI: 10.1016/S0010-938X(97)83355-0.
- (76) Sainz-Rosales, A.; Ocampo-Lazcarro, X.; Hernández-Pérez, A.; González-Gutiérrez, A. G.; Larios-Durán, E. R.; Ponce de León, C.; Walsh, F. C.; Bárcena-Soto, M.; Casillas, N. Classic Evans's Drop Corrosion Experiment Investigated in Terms of a Tertiary Current and Potential Distribution. *CMD* **2022**, *3* (2), 270–280. DOI: 10.3390/cmd3020016.
- (77) Guerra-Camacho, L.; Ruiz-Garcia, A.; Godínez, F. A.; Genesca, J.; Terryn, H.; Montoya, R. Influence of convection during droplet evaporation on corrosion product distribution in CFRP-AA2024 galvanic couple: Modeling and experimental approaches. *Corrosion Science* **2024**, *240*, 112462. DOI: 10.1016/j.corsci.2024.112462.
- (78) Tsuru, T.; Tamiya, K.-I.; Nishikata, A. Formation and growth of micro-droplets during the initial stage of atmospheric corrosion. *Electrochimica Acta* **2004**, *49* (17-18), 2709–2715. DOI: 10.1016/j.electacta.2004.01.032.
- (79) Gateman, S. M.; Gharbi, O.; Turmine, M.; Vivier, V. Measuring changes in wettability and surface area during micro droplet corrosion measurements. *Electrochimica Acta* **2021**, *399*, 139402. DOI: 10.1016/j.electacta.2021.139402.
- (80) Street, S. R.; Cook, A. J.; Mohammed-Ali, H. B.; Rayment, T.; Davenport, A. J. The Effect of Deposition Conditions on Atmospheric Pitting Corrosion Location Under Evans Droplets on Type 304L Stainless Steel. *CORROSION* **2018**, *74* (5), 520–529. DOI: 10.5006/2614.
- (81) Butt, H.-J.; Kappl, M. *Surface and interfacial forces*; Physics textbook; Wiley-VCH, 2010. ISBN: 978-3-527-40849-8.
- (82) Bram, C.; Jung, C.; Stratmann, M. Self assembled molecular monolayers on oxidized inhomogeneous aluminum surfaces. *Fresenius' Journal of Analytical Chemistry* **1997**, *358* (1-2), 108–111. DOI: 10.1007/s002160050357.

- (83) Hosseinpour, S.; Johnson, C. M.; Leygraf, C. Alkanethiols as Inhibitors for the Atmospheric Corrosion of Copper Induced by Formic Acid: Effect of Chain Length. *J. Electrochem. Soc.* **2013**, *160* (6), C270–C276. DOI: 10.1149/2.104306jes.
- (84) Zhao, W.; Chang, T.; Leygraf, C.; Johnson, C. M. Corrosion inhibition of copper with octadecylphosphonic acid (ODPA) in a simulated indoor atmospheric environment. *Corrosion Science* **2021**, *192*, 109777. DOI: 10.1016/j.corsci.2021.109777.
- (85) Maxisch, M.; Thissen, P.; Giza, M.; Grundmeier, G. Interface chemistry and molecular interactions of phosphonic acid self-assembled monolayers on oxyhydroxide-covered aluminum in humid environments. *Langmuir : the ACS journal of surfaces and colloids* **2011**, *27* (10), 6042–6048. DOI: 10.1021/la200445x.
- (86) Hintze, P. E.; Calle, L. M. Electrochemical properties and corrosion protection of organosilane self-assembled monolayers on aluminum 2024-T3. *Electrochimica Acta* **2006**, *51* (8–9), 1761–1766. DOI: 10.1016/j.electacta.2005.02.147.
- (87) Semiletov, A. M.; Kudelina, A. A.; Kuznetsov, Y. I. Super Hydrophobization of the Surface of Aluminum Alloy with Organic Acids to Protect Against Atmospheric Corrosion. *Russ. J. Phys. Chem.* **2023**, *97* (2), 397–404. DOI: 10.1134/S0036024423020243.
- (88) Wang, P.; Zhang, D.; Lu, Z. Advantage of super-hydrophobic surface as a barrier against atmospheric corrosion induced by salt deliquescence. *Corrosion Science* **2015**, *90*, 23–32. DOI: 10.1016/j.corsci.2014.09.001.
- (89) Liu, X.; Wang, P.; Zhang, D.; Chen, X. Atmospheric Corrosion Protection Performance and Mechanism of Superhydrophobic Surface Based on Coalescence-Induced Droplet Self-Jumping Behavior. *ACS applied materials & interfaces* **2021**, *13* (21), 25438–25450. DOI: 10.1021/acsami.0c21802.
- (90) Khan, M. A.; Jappes, J. T. W., Eds. *Innovations in Additive Manufacturing*, 1st ed. 2022; Springer Tracts in Additive Manufacturing; Springer International Publishing; Imprint Springer, 2022. DOI: 10.1007/978-3-030-89401-6.
- (91) Sander, G.; Tan, J.; Balan, P.; Gharbi, O.; Feenstra, D. R.; Singer, L.; Thomas, S.; Kelly, R. G.; Scully, J. R.; Birbilis, N. Corrosion of Additively Manufactured Alloys: A Review. *CORROSION* **2018**, *74* (12), 1318–1350. DOI: 10.5006/2926.
- (92) Zhang, F.; Liu, Z.; Pan, C.; Deng, Y.; Xia, D.-H.; Tribollet, B. Effect of Si network continuity on the localized corrosion of AlSi10Mg alloy fabricated by selective laser melting. *Corrosion Science* **2025**, *257*, 113336. DOI: 10.1016/j.corsci.2025.113336.
- (93) Pech-Canul, M. A.; Pech-Canul, M. I.; Bartolo-Pérez, P.; Echeverría, M. The role of silicon alloying addition on the pitting corrosion resistance of an Al-12wt.%Si alloy. *Electrochimica Acta* **2014**, *140*, 258–265. DOI: 10.1016/j.electacta.2014.05.034.
- (94) Örneke, C. Additive manufacturing – a general corrosion perspective. *Corrosion Engineering, Science and Technology* **2018**, *53* (7), 531–535. DOI: 10.1080/1478422X.2018.1511327.
- (95) Suryawanshi, J.; Baskaran, T.; Prakash, O.; Arya, S. B.; Ramamurty, U. On the corrosion resistance of some selective laser melted alloys. *Materialia* **2018**, *3*, 153–161. DOI: 10.1016/j.mtla.2018.08.022.
- (96) Revilla, R. I.; Terryn, H.; Graeve, I. de. Growth kinetics and passive behavior of the native oxide film on additively manufactured AlSi10Mg versus the conventional cast alloy. *Corrosion Science* **2022**, *203*, 110352. DOI: 10.1016/j.corsci.2022.110352.
- (97) Hoshi, Y.; Miyazawa, R.; Otani, Y.; Kim, D.; Takata, N.; Kobashi, M. Four-dimensional electrochemical impedance spectroscopy: Role of microstructure on corrosion behaviour of Al-Si alloys additive-manufactured by laser powder bed fusion. *Corrosion Science* **2024**, *232*, 112018. DOI: 10.1016/j.corsci.2024.112018.

- (98) Zhang, Z.; Zhao, Z.; Li, X.; Wang, B.; Bai, P. Effect of Direct Aging on Corrosion Behavior of AlSi10Mg Alloy Fabricated by Laser Powder Bed Fusion. *Acta Metall. Sin. (Engl. Lett.)* **2023**. DOI: 10.1007/s40195-023-01628-2.
- (99) Zhang, Z.; Wang, B.; Zhao, Z.; Li, X.; Liu, B.; Bai, P. Effect of chloride ion concentration on corrosion process of selective laser melted AlSi10Mg with different heat treatments studied by electrochemical noise. *Journal of Materials Research and Technology* **2022**, *16*, 1597–1609. DOI: 10.1016/j.jmrt.2021.12.102.
- (100) Gu, X.-H.; Zhang, J.-X.; Fan, X.-L.; Zhang, L.-C. Corrosion Behavior of Selective Laser Melted AlSi10Mg Alloy in NaCl Solution and Its Dependence on Heat Treatment. *Acta Metall. Sin. (Engl. Lett.)* **2020**, *33* (3), 327–337. DOI: 10.1007/s40195-019-00903-5.
- (101) Cabrini, M.; Lorenzi, S.; Pastore, T.; Pellegrini, S.; Pavese, M.; Fino, P.; Ambrosio, E. P.; Calignano, F.; Manfredi, D. Corrosion resistance of direct metal laser sintering AlSiMg alloy. *Surf. Interface Anal.* **2016**, *48* (8), 818–826. DOI: 10.1002/sia.5981.
- (102) Wu, J.; Wang, X. Q.; Wang, W.; Attallah, M. M.; Loretto, M. H. Microstructure and strength of selectively laser melted AlSi10Mg. *Acta Materialia* **2016**, *117*, 311–320. DOI: 10.1016/j.actamat.2016.07.012.
- (103) Leon, A.; Aghion, E. Effect of surface roughness on corrosion fatigue performance of AlSi10Mg alloy produced by Selective Laser Melting (SLM). *Materials Characterization* **2017**, *131*, 188–194. DOI: 10.1016/j.matchar.2017.06.029.
- (104) Runge, J. M. *The metallurgy of anodizing aluminum: Connecting science to practice*; Springer, 2018. ISBN: 978-3-319-72177-4. DOI: 10.1007/978-3-319-72177-4.
- (105) Kurita, H.; Tako, S.; Tanaka, C.; Hara, K.; Matsushima, K.; Satsukawa, K.; Watanabe, K.; Kyogoku, H. Anodizing 3D-Printed AlSi10Mg Alloy and Its Fatigue Properties. *Metals* **2025**, *15* (9), 1022. DOI: 10.3390/met15091022.
- (106) Walton, J. W.; Dwyer, J. H.; Rice, L.; Rueger, Z.; Swain, G. M. The Effect of Sulfuric Acid Anodization on the Electrochemical Properties of Aluminum Alloy AlSi 10 Mg Prepared by Selective Laser Melting. *J. Electrochem. Soc.* **2024**, *171* (5), 51503. DOI: 10.1149/1945-7111/ad45c5.
- (107) Gamba, M.; Cristoforetti, A.; Fedel, M.; Ceriani, F.; Ormellese, M.; Brenna, A. Plasma Electrolytic Oxidation (PEO) coatings on aluminum alloy 2024: A review of mechanisms, processes, and corrosion resistance enhancement. *Applied Surface Science Advances* **2025**, *26*, 100707. DOI: 10.1016/j.apsadv.2025.100707.
- (108) Li, Z.; Kou, R.; Ma, G.; Wang, J.; Chen, S.; Liu, G.; Zhang, Y. Corrosion behavior analysis and plasma electrolytic oxidation coatings protection study of selective laser melting–AlSi10Mg alloy. *Surface and Coatings Technology* **2025**, *516*, 132753. DOI: 10.1016/j.surfcoat.2025.132753.
- (109) Pezzato, L.; Dabalà, M.; Gross, S.; Brunelli, K. Effect of microstructure and porosity of AlSi10Mg alloy produced by selective laser melting on the corrosion properties of plasma electrolytic oxidation coatings. *Surface and Coatings Technology* **2020**, *404*, 126477. DOI: 10.1016/j.surfcoat.2020.126477.
- (110) Pezzato, L.; Gennari, C.; Franceschi, M.; Brunelli, K. Influence of silicon morphology on direct current plasma electrolytic oxidation process in AlSi10Mg alloy produced with laser powder bed fusion. *Scientific reports* **2022**, *12* (1), 14329. DOI: 10.1038/s41598-022-18176-x.
- (111) Akbarzadeh, S.; Paint, Y.; Olivier, M.-G. A comparative study of different sol-gel coatings for sealing the plasma electrolytic oxidation (PEO) layer on AA2024 alloy. *Electrochimica Acta* **2023**, *443*, 141930. DOI: 10.1016/j.electacta.2023.141930.
- (112) Figueira, R. B. Hybrid Sol-gel Coatings for Corrosion Mitigation: A Critical Review. *Polymers* **2020**, *12* (3). DOI: 10.3390/polym12030689.

- (113) Macera, L.; Pullini, D.; Boschetto, A.; Bottini, L.; Mingazzini, C.; Falletti, G. L. Sol–Gel Silica Coatings for Corrosion Protection of Aluminum Parts Manufactured by Selective Laser Melting (SLM) Technology. *Coatings* **2023**, *13* (6), 1081. DOI: 10.3390/coatings13061081.
- (114) Spuller, M.; Kovač, N.; Rodič, P.; Chwatal, S.; Cabrioli, M.; Vanazzi, M.; Pasquale, G. de; Lackner, J. M.; Kaindl, R.; Waldhauser, W. The effect of plasma-polymerized cerium-doped hexamethyldisiloxane film thickness on corrosion protection of L-PBF AlSi10Mg. *Monatsh Chem* **2025**. DOI: 10.1007/s00706-025-03408-3.
- (115) Prüßner, T.; Hoyer, K.-P.; Buitkamp, N.; Vieth, P.; Grundmeier, G. Surface functionalisation of additively manufactured AlSi10Mg by organophosphonic acid and PDMS grafting. *Materials Chemistry and Physics* **2026**, *349*, 131758. DOI: 10.1016/j.matchemphys.2025.131758.
- (116) Weißbach, W.; Dahms, M.; Jaroschek, C. *Werkstoffe und ihre Anwendungen*; Springer Fachmedien Wiesbaden, 2018. DOI: 10.1007/978-3-658-19892-3.
- (117) UA Marketing. *Understanding Aluminum Alloy Numbering and Groups*. <https://unitedaluminum.com/understanding-aluminum-alloy-numbering-and-groups/> (accessed 2026-02-27).
- (118) Rambabu, P.; Eswara Prasad, N.; Kutumbarao, V. V.; Wanhill, R. J. H. Aluminium Alloys for Aerospace Applications. In *Aerospace Materials and Material Technologies*; Prasad, N. E., Wanhill, R. J. H., Eds.; Indian Institute of Metals Series; Springer Singapore, 2017; pp 29–52. DOI: 10.1007/978-981-10-2134-3_2.
- (119) Boag, A.; Hughes, A. E.; Wilson, N. C.; Torpy, A.; MacRae, C. M.; Glenn, A. M.; Muster, T. H. How complex is the microstructure of AA2024-T3? *Corrosion Science* **2009**, *51* (8), 1565–1568. DOI: 10.1016/j.corsci.2009.05.001.
- (120) Huang, K., Ed. *Principles of Electrochemical Conversion and Storage Devices*; Wiley, 2025. DOI: 10.1002/9783527851638.
- (121) Boag, A.; Hughes, A. E.; Glenn, A. M.; Muster, T. H.; McCulloch, D. Corrosion of AA2024-T3 Part I: Localised corrosion of isolated IM particles. *Corrosion Science* **2011**, *53* (1), 17–26. DOI: 10.1016/j.corsci.2010.09.009.
- (122) Cavanaugh, M. K.; Li, J.-C.; Birbilis, N.; Buchheit, R. G. Electrochemical Characterization of Intermetallic Phases Common to Aluminum Alloys as a Function of Solution Temperature. *J. Electrochem. Soc.* **2014**, *161* (12), C535–C543. DOI: 10.1149/2.0361412jes.
- (123) Peltier, F.; Thierry, D. Review of Cr-Free Coatings for the Corrosion Protection of Aluminum Aerospace Alloys. *Coatings* **2022**, *12* (4), 518. DOI: 10.3390/coatings12040518.
- (124) Zhao, J.; Xia, L.; Sehgal, A.; Lu, D.; McCreery, R. L.; Frankel, G. S. Effects of chromate and chromate conversion coatings on corrosion of aluminum alloy 2024-T3. *Surface and Coatings Technology* **2001**, *140* (1), 51–57. DOI: 10.1016/S0257-8972(01)01003-9.
- (125) Terada, M.; Queiroz, F. M.; Aguiar, D.; Ayusso, V. H.; Costenaro, H.; Olivier, M.-G.; Melo, H. G. de; Costa, I. Corrosion resistance of tartaric-sulfuric acid anodized AA2024-T3 sealed with Ce and protected with hybrid sol–gel coating. *Surface and Coatings Technology* **2019**, *372*, 422–426. DOI: 10.1016/j.surfcoat.2019.05.028.
- (126) Capelossi, V. R.; Poelman, M.; Recloux, I.; Hernandez, R.; Melo, H. G. de; Olivier, M. G. Corrosion protection of clad 2024 aluminum alloy anodized in tartaric-sulfuric acid bath and protected with hybrid sol–gel coating. *Electrochimica Acta* **2014**, *124*, 69–79. DOI: 10.1016/j.electacta.2013.09.004.
- (127) Prada Ramirez, O. M.; Kremmer, T. M.; Marin, J. H.; Da Silva, B. P.; Strykevich, M.; Tunes, M. A.; Ferreira, M.; Aoki, I. V.; Ando, R. A.; Pogatscher, S.; Melo, H. G. de. Ce nanoparticles and sol-gel hybrid organic-inorganic coatings maximize corrosion protection in the anodized AA2024-T3. *Corrosion Science* **2023**, *221*, 111330. DOI: 10.1016/j.corsci.2023.111330.

- (128) Yasakau, K. A.; Zheludkevich, M. L.; Lamaka, S. V.; Ferreira, M. G. S. Mechanism of corrosion inhibition of AA2024 by rare-earth compounds. *J. Phys. Chem. B* **2006**, *110* (11), 5515–5528. DOI: 10.1021/jp0560664.
- (129) Li, Z.; Visser, P.; Hughes, A. E.; Homborg, A.; Gonzalez-Garcia, Y.; Mol, A. Review of the state of art of Li-based inhibitors and coating technology for the corrosion protection of aluminium alloys. *Surface and Coatings Technology* **2024**, *478*, 130441. DOI: 10.1016/j.surfcoat.2024.130441.
- (130) Spori, D. M.; Venkataraman, N. V.; Tosatti, S. G. P.; Durmaz, F.; Spencer, N. D.; Zürcher, S. Influence of alkyl chain length on phosphate self-assembled monolayers. *Langmuir : the ACS journal of surfaces and colloids* **2007**, *23* (15), 8053–8060. DOI: 10.1021/la700474v.
- (131) Dietrich, H.; Zahn, D. Molecular Mechanisms of Solvent-Controlled Assembly of Phosphonate Monolayers on Oxide Surfaces. *J. Phys. Chem. C* **2017**, *121* (33), 18012–18020. DOI: 10.1021/acs.jpcc.7b05750.
- (132) Marinova, K. G.; Christova, D.; Tcholakova, S.; Efremov, E.; Denkov, N. D. Hydrophobization of glass surface by adsorption of poly(dimethylsiloxane). *Langmuir : the ACS journal of surfaces and colloids* **2005**, *21* (25), 11729–11737. DOI: 10.1021/la051690t.
- (133) Stöber, W.; Fink, A.; Bohn, E. Controlled growth of monodisperse silica spheres in the micron size range. *Journal of Colloid and Interface Science* **1968**, *26* (1), 62–69. DOI: 10.1016/0021-9797(68)90272-5.
- (134) Oh, J.; Imai, H.; Hirashima, H. Direct deposition of silica films using silicon alkoxide solution. *Journal of Non-Crystalline Solids* **1998**, *241* (2-3), 91–97. DOI: 10.1016/S0022-3093(98)00772-8.
- (135) Issa, A. A.; Luyt, A. S. Kinetics of Alkoxysilanes and Organoalkoxysilanes Polymerization: A Review. *Polymers* **2019**, *11* (3). DOI: 10.3390/polym11030537.
- (136) Kákoš, J.; Mikula, M.; Harmatha, L. Ultrathin insulating silica layers prepared from adsorbed TEOS, H₂O and NH₃ as a catalyst. *Microelectronics Journal* **2008**, *39* (12), 1626–1628. DOI: 10.1016/j.mejo.2008.02.008.
- (137) B. Arkles. *Hydrophobicity, Hydrophilicity and Silanes*. www.pcimag.com (accessed 2026-05-08).
- (138) Deng, X.; Mammen, L.; Butt, H.-J.; Vollmer, D. Candle soot as a template for a transparent robust superamphiphobic coating. *Science (New York, N.Y.)* **2012**, *335* (6064), 67–70. DOI: 10.1126/science.1207115.
- (139) Bryant, W. A. The fundamentals of chemical vapour deposition. *J Mater Sci* **1977**, *12* (7), 1285–1306. DOI: 10.1007/BF00540843.
- (140) López, A. J.; Ureña, A.; López, M. D.; Rams, J. Protection against corrosion of aluminium-SiC composites by sol-gel silica coatings. *Surface and Coatings Technology* **2008**, *202* (16), 3755–3763. DOI: 10.1016/j.surfcoat.2007.12.043.
- (141) Grundmeier, G.; Keudell, A. von; los Arcos, T. de. Fundamentals and Applications of Reflection FTIR Spectroscopy for the Analysis of Plasma Processes at Materials Interfaces. *Plasma Processes & Polymers* **2015**, *12* (9), 926–940. DOI: 10.1002/ppap.201500087.
- (142) Golden, W. G.; Saperstein, D. D.; Severson, M. W.; Overend, J. Infrared reflection-absorption spectroscopy of surface species: a comparison of Fourier transform and dispersion methods. *J. Phys. Chem.* **1984**, *88* (3), 574–580. DOI: 10.1021/j150647a049.
- (143) Moskovits, M. Surface selection rules. *The Journal of chemical physics* **1982**, *77* (9), 4408–4416. DOI: 10.1063/1.444442.
- (144) Su, Z.-F.; Chen, A.-C.; Lipkowski, J. PM IRRAS Studies of Organized Molecular Films at a Gold Electrode Surface. *Journal of Electrochemistry* **2025**, *31* (6). DOI: 10.61558/2993-074X.3528.

- (145) Bordo, V. G.; Rubahn, H.-G. *Optics and Spectroscopy at Surfaces and Interfaces*; Wiley, 2005. DOI: 10.1002/9783527618699.
- (146) Pinder, J. W.; Major, G. H.; Baer, D. R.; Terry, J.; Whitten, J. E.; Čechal, J.; Crossman, J. D.; Lizarbe, A. J.; Jafari, S.; Easton, C. D.; Baltrusaitis, J.; van Spronsen, M. A.; Linford, M. R. Avoiding common errors in X-ray photoelectron spectroscopy data collection and analysis, and properly reporting instrument parameters. *Applied Surface Science Advances* **2024**, *19*, 100534. DOI: 10.1016/j.apsadv.2023.100534.
- (147) Brundle, C. R.; Crist, B. V. X-ray photoelectron spectroscopy: A perspective on quantitation accuracy for composition analysis of homogeneous materials. *Journal of Vacuum Science & Technology A* **2020**, *38* (4). DOI: 10.1116/1.5143897.
- (148) Krishna, D. N. G.; Philip, J. Review on surface-characterization applications of X-ray photoelectron spectroscopy (XPS): Recent developments and challenges. *Applied Surface Science Advances* **2022**, *12*, 100332. DOI: 10.1016/j.apsadv.2022.100332.
- (149) Shard, A. G. Practical guides for x-ray photoelectron spectroscopy: Quantitative XPS. *Journal of Vacuum Science & Technology A* **2020**, *38* (4). DOI: 10.1116/1.5141395.
- (150) Strohmeier, B. R. An ESCA method for determining the oxide thickness on aluminum alloys. *Surf. Interface Anal.* **1990**, *15* (1), 51–56. DOI: 10.1002/sia.740150109.
- (151) Aoyagi, S. Time-of-Flight Secondary Ion Mass Spectrometry. In *Compendium of Surface and Interface Analysis*; Japa, T. S. S. S. o., Ed.; Springer Singapore, 2018; pp 725–731. DOI: 10.1007/978-981-10-6156-1_117.
- (152) Vickerman, J. C., Ed. *Surface analysis: The principal techniques*, 2. ed.; Wiley, 2009, ISBN: 978-0-470-01763-0.
- (153) Egerton, R. *Physical principles of electron microscopy: An introduction to TEM, SEM, and AEM*; Springer, 2005, ISBN: 0-387-25800-0.
- (154) Murphy, D. B.; Davidson, M. W. *Fundamentals of light microscopy and electronic imaging*, 2nd edition; Wiley-Blackwell, 2013. DOI: 10.1002/9781118382905.
- (155) *Geometrical Product Specifications (GPS) - Surface texture: Profile method - Terms, definitions and surface texture parameters: ISO 21920-2:2021*, 2021.
- (156) Hübschen, G.; Altpeter, I.; Tschuncky, R.; Herrmann, H.-G., Eds. *Materials characterization using nondestructive evaluation (NDE) methods*; Woodhead Publishing series in electronic and optical materials, number 88; Elsevier/WP Woodhead Publishing, 2016. DOI: 10.1016/C2014-0-00661-2. DOI: 10.1016/C2014-0-00661-2.
- (157) Ando, T. *High-speed atomic force microscopy in biology: Directly watching dynamics of biomolecules in action*; NanoScience and Technology; Springer, 2022. ISBN: 9783662647837.
- (158) Örneke, C.; Leygraf, C.; Pan, J. On the Volta potential measured by SKPFM – fundamental and practical aspects with relevance to corrosion science. *Corrosion Engineering, Science and Technology* **2019**, *54* (3), 185–198. DOI: 10.1080/1478422X.2019.1583436.
- (159) Holze, R. C.M.A. Brett, A.M.O. Brett: Electrochemistry — Principles, methods and applications, Oxford University Press, Oxford, ISBN 0-19-855388-9, 1993, 427 pages, £ 25.00. *Ber Bunsenges Phys Chem* **1994**, *98* (10), 1350. DOI: 10.1002/bbpc.19940981033.
- (160) Marcus, P. *Corrosion Mechanisms in Theory and Practice*; CRC Press, 2011. DOI: 10.1201/b11020.
- (161) Mirhashemihaghighi, S.; Światowska, J.; Maurice, V.; Seyeux, A.; Klein, L. H.; Härkönen, E.; Ritala, M.; Marcus, P. Electrochemical and Surface Analysis of the Corrosion Protection of Copper by Nanometer-Thick Alumina Coatings Prepared by Atomic Layer Deposition. *J. Electrochem. Soc.* **2015**, *162* (8), C377–C384. DOI: 10.1149/2.0081508jes.

- (162) Hirschorn, B.; Orazem, M. E.; Tribollet, B.; Vivier, V.; Frateur, I.; Musiani, M. Determination of effective capacitance and film thickness from constant-phase-element parameters. *Electrochimica Acta* **2010**, 55 (21), 6218–6227. DOI: 10.1016/j.electacta.2009.10.065.
- (163) Brug, G. J.; van den Eeden, A.; Sluyters-Rehbach, M.; Sluyters, J. H. The analysis of electrode impedances complicated by the presence of a constant phase element. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, 176 (1-2), 275–295. DOI: 10.1016/S0022-0728(84)80324-1.
- (164) Butt, H.-J.; Graf, K.; Kappl, M. *Physics and chemistry of interfaces*; Physics textbook; Wiley-VCH, 2003. DOI: 10.1002/3527602313.
- (165) R. Lindström, L.-G. Johansson, J.-E. Svensson. The influence of NaCl and CO₂ on the atmospheric corrosion of magnesium alloy AZ91. *Materials and Corrosion* **2003** (54), 587–594. DOI: 10.1002/maco.200390130.
- (166) Buffeteau, T.; Desbat, B.; Turlet, J. M. Polarization Modulation FT-IR Spectroscopy of Surfaces and Ultra-Thin Films: Experimental Procedure and Quantitative Analysis. *Appl Spectrosc* **1991**, 45 (3), 380–389. DOI: 10.1366/0003702914337308.
- (167) Wertheim, G. K. Deconvolution and smoothing: Applications in ESCA. *Journal of Electron Spectroscopy and Related Phenomena* **1975**, 6 (3), 239–251. DOI: 10.1016/0368-2048(75)80019-3.
- (168) Shirley, D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Phys. Rev. B* **1972**, 5 (12), 4709–4714. DOI: 10.1103/PhysRevB.5.4709.
- (169) Boukamp, B. A. A Linear Kronig-Kramers Transform Test for Immittance Data Validation. *J. Electrochem. Soc.* **1995**, 142 (6), 1885–1894. DOI: 10.1149/1.2044210.
- (170) Prüßner, T.; Hoyer, K.-P.; Buitkamp, N.; Grundmeier, G. Atmospheric Corrosion Protection of LPBF Manufactured AlSi10Mg by Combining SiO_x-CVD and PDMS Grafting. *Materials and Corrosion* **2026**. DOI: 10.1002/maco.70163.
- (171) Justin Gorham. *NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20, National Institute of Standards and Technology, Gaithersburg MD, 20899 (2000)*, DOI: <https://dx.doi.org/10.18434/T4T88K>, (retrieved 09.05.2025).
- (172) Lee, A. Y.; Powell, C. J.; Gorham, J. M.; Morey, A.; Scott, J. H. J.; Hanisch, R. J. Development of the NIST X-ray Photoelectron Spectroscopy (XPS) Database, Version 5. *CODATA* **2024**, 23, 45. DOI: 10.5334/dsj-2024-045.
- (173) Barr, T. L.; Seal, S.; Chen, L. M.; Kao, C. C. A new interpretation of the binding energies in X-ray photoelectron studies of oxides. *Thin Solid Films* **1994**, 253 (1-2), 277–284. DOI: 10.1016/0040-6090(94)90334-4.
- (174) Biesinger, M. C. Accessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: Insights from a multi-user facility data review. *Applied Surface Science* **2022**, 597, 153681. DOI: 10.1016/j.apsusc.2022.153681.
- (175) Scott, P. R.; Wieliczka, D. M.; Kruger, M. B. Depth Profiled XPS Analysis of a Polymerized Silicon-Carbon Thin Film. *Plasma Chem Plasma Process* **2009**, 29 (6), 559–566. DOI: 10.1007/s11090-009-9197-8.
- (176) Sharma, V.; Dhayal, M.; Govind; Shivaprasad, S. M.; Jain, S. C. Surface characterization of plasma-treated and PEG-grafted PDMS for micro fluidic applications. *Vacuum* **2007**, 81 (9), 1094–1100. DOI: 10.1016/j.vacuum.2007.02.004.
- (177) Pellerite, M. J.; Dunbar, T. D.; Boardman, L. D.; Wood, E. J. Effects of Fluorination on Self-Assembled Monolayer Formation from Alkanephosphonic Acids on Aluminum: Kinetics and Structure. *J. Phys. Chem. B* **2003**, 107 (42), 11726–11736. DOI: 10.1021/jp0354200.
- (178) Dölle, C.; Papmeyer, M.; Ott, M.; Vissing, K. Gradual photochemical-induced conversion of liquid polydimethylsiloxane layers to carbon containing silica coatings by VUV irradiation at 172

nm. *Langmuir : the ACS journal of surfaces and colloids* **2009**, 25 (12), 7129–7134. DOI: 10.1021/la900278t.

(179) Elzein, T.; Galliano, A.; Bistac, S. Chains anisotropy in PDMS networks due to friction on gold surfaces. *J Polym Sci B Polym Phys* **2004**, 42 (12), 2348–2353. DOI: 10.1002/polb.20054.

(180) Maxisch, M.; Ebbert, C.; Torun, B.; Fink, N.; los Arcos, T. de; Lackmann, J.; Maier, H. J.; Grundmeier, G. PM-IRRAS studies of the adsorption and stability of organophosphonate monolayers on passivated NiTi surfaces. *Applied Surface Science* **2011**, 257 (6), 2011–2018. DOI: 10.1016/j.apsusc.2010.09.044.

(181) Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. Fundamental studies of microscopic wetting on organic surfaces. 1. Formation and structural characterization of a self-consistent series of polyfunctional organic monolayers. *J. Am. Chem. Soc.* **1990**, 112 (2), 558–569. DOI: 10.1021/ja00158a012.

(182) Byrd, H.; Pike, J. K.; Talham, D. R. Inorganic monolayers formed at an organic template: a Langmuir-Blodgett route to monolayer and multilayer films of zirconium octadecylphosphonate. *Chem. Mater.* **1993**, 5 (5), 709–715. DOI: 10.1021/cm00029a023.

(183) Thissen, P.; Valtiner, M.; Grundmeier, G. Stability of phosphonic acid self-assembled monolayers on amorphous and single-crystalline aluminum oxide surfaces in aqueous solution. *Langmuir : the ACS journal of surfaces and colloids* **2010**, 26 (1), 156–164. DOI: 10.1021/la900935s.

(184) Fondeur, F.; Koenig, J. L. FT-IR Characterization of the Surface of Aluminum as a Result of Chemical Treatment. *The Journal of Adhesion* **1993**, 40 (2-4), 189–205. DOI: 10.1080/00218469308031284.

(185) los Arcos, T. de; Müller, H.; Wang, F.; Damerla, V. R.; Hoppe, C.; Weinberger, C.; Tiemann, M.; Grundmeier, G. Review of infrared spectroscopy techniques for the determination of internal structure in thin SiO₂ films. *Vibrational Spectroscopy* **2021**, 114, 103256. DOI: 10.1016/j.vibspec.2021.103256.

(186) Cai, D.; Neyer, A.; Kuckuk, R.; Heise, H. M. Raman, mid-infrared, near-infrared and ultraviolet–visible spectroscopy of PDMS silicone rubber for characterization of polymer optical waveguide materials. *Journal of Molecular Structure* **2010**, 976 (1-3), 274–281. DOI: 10.1016/j.molstruc.2010.03.054.

(187) Baer, D. R.; Artyushkova, K.; Cohen, H.; Easton, C. D.; Engelhard, M.; Gengenbach, T. R.; Greczynski, G.; Mack, P.; Morgan, D. J.; Roberts, A. XPS guide: Charge neutralization and binding energy referencing for insulating samples. *Journal of Vacuum Science & Technology A* **2020**, 38 (3). DOI: 10.1116/6.0000057.

(188) Greczynski, G.; Hultman, L. Reliable determination of chemical state in x-ray photoelectron spectroscopy based on sample-work-function referencing to adventitious carbon: Resolving the myth of apparent constant binding energy of the C 1s peak. *Applied Surface Science* **2018**, 451, 99–103. DOI: 10.1016/j.apsusc.2018.04.226.

(189) Greczynski, G.; Hultman, L. Compromising Science by Ignorant Instrument Calibration-Need to Revisit Half a Century of Published XPS Data. *Angewandte Chemie (International ed. in English)* **2020**, 59 (13), 5002–5006. DOI: 10.1002/anie.201916000.

(190) Gross, T.; Ramm, M.; Sonntag, H.; Unger, W.; Weijers, H. M.; Adem, E. H. An XPS analysis of different SiO₂ modifications employing a C 1s as well as an Au 4f 7/2 static charge reference. *Surface & Interface Analysis* **1992**, 18 (1), 59–64. DOI: 10.1002/sia.740180110.

(191) Hughes, A. E.; Hedges, M. M.; Sexton, B. A. Reactions at the Al/SiO₂/SiC layered interface. *J Mater Sci* **1990**, 25 (11), 4856–4865. DOI: 10.1007/BF01129953.

(192) C. J. Powell and A. Jablonski. *NIST Electron Inelastic-Mean-Free-Path Database*, Version 1.2; MD, 2010. DOI: 10.18434/T48C78.

- (193) Zakay, A.; Aghion, E. Effect of Post-heat Treatment on the Corrosion Behavior of AlSi10Mg Alloy Produced by Additive Manufacturing. *JOM* **2019**, *71* (3), 1150–1157. DOI: 10.1007/s11837-018-3298-x.
- (194) Kubacki, G. W.; Brownhill, J. P.; Kelly, R. G. Comparison of Atmospheric Corrosion of Additively Manufactured and Cast Al-10Si-Mg Over a Range of Heat Treatments. *CORROSION* **2019**, *75* (12), 1527–1540. DOI: 10.5006/3318.
- (195) Lu, Z.; Wang, P.; Zhang, D. Super-hydrophobic film fabricated on aluminium surface as a barrier to atmospheric corrosion in a marine environment. *Corrosion Science* **2015**, *91*, 287–296. DOI: 10.1016/j.corsci.2014.11.029.
- (196) Kozlica, D. K.; Izquierdo, J.; Souto, R. M.; Milošev, I. Inhibition of the localised corrosion of AA2024 in chloride solution by 2-mercaptobenzimidazole and octylphosphonic acid. *npj Mater Degrad* **2023**, *7* (1). DOI: 10.1038/s41529-023-00368-z.
- (197) Hosseinpour, S.; Forslund, M.; Johnson, C. M.; Pan, J.; Leygraf, C. Atmospheric corrosion of Cu, Zn, and Cu–Zn alloys protected by self-assembled monolayers of alkanethiols. *Surface Science* **2016**, *648*, 170–176. DOI: 10.1016/j.susc.2015.10.045.
- (198) Schnieders, H.; Ozcan, O.; Grundmeier, G. Self-localization of mixed organophosphonic acid and organothiol monolayers on patterned Al–Cu substrates. *Applied Surface Science* **2013**, *287*, 397–403. DOI: 10.1016/j.apsusc.2013.09.166.
- (199) Hauffman, T.; Hubin, A.; Terryn, H. Study of the self-assembling of n-octylphosphonic acid layers on aluminum oxide from ethanolic solutions. *Surface & Interface Analysis* **2013**, *45* (10), 1435–1440. DOI: 10.1002/sia.5150.
- (200) Zhao, W.; Göthelid, M.; Hosseinpour, S.; Johansson, M. B.; Li, G.; Leygraf, C.; Johnson, C. M. The nature of self-assembled octadecylphosphonic acid (ODPA) layers on copper substrates. *Journal of Colloid and Interface Science* **2021**, *581* (Pt B), 816–825. DOI: 10.1016/j.jcis.2020.07.058.
- (201) Sang, L.; Mudalige, A.; Sigdel, A. K.; Giordano, A. J.; Marder, S. R.; Berry, J. J.; Pemberton, J. E. PM-IRRAS Determination of Molecular Orientation of Phosphonic Acid Self-Assembled Monolayers on Indium Zinc Oxide. *Langmuir : the ACS journal of surfaces and colloids* **2015**, *31* (20), 5603–5613. DOI: 10.1021/acs.langmuir.5b00129.
- (202) Alwis, C. de; Leftwich, T. R.; Perrine, K. A. New Approach to Simultaneous In Situ Measurements of the Air/Liquid/Solid Interface Using PM-IRRAS. *Langmuir : the ACS journal of surfaces and colloids* **2020**, *36* (13), 3404–3414. DOI: 10.1021/acs.langmuir.9b03958.
- (203) Borah, B.; Rajitha, G.; Dash, R. K. Correlation between the thickness and properties of the ethanol treated GO–PDMS based composite materials. *J Mater Sci: Mater Electron* **2018**, *29* (23), 20216–20224. DOI: 10.1007/s10854-018-0154-2.
- (204) Ohuchi, F. S. Chemical bonding and electronic structures of the Al₂SiO₅ polymorphs, andalusite, sillimanite, and kyanite: X-ray photoelectron- and electron energy loss spectroscopy studies. *American Mineralogist* **2006**, *91* (5-6), 740–746. DOI: 10.2138/am.2006.1887.
- (205) Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of electron inelastic mean free paths (IMFPs). IV. Evaluation of calculated IMFPs and of the predictive IMFP formula TPP-2 for electron energies between 50 and 2000 eV. *Surface & Interface Analysis* **1993**, *20* (1), 77–89. DOI: 10.1002/sia.740200112.

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9.3. Declaration on the use of generative AI and AI-assisted technologies

During the preparation of this dissertation, I, Tim Hendrik Prüßner, used AI-assisted tools in a supporting capacity. DeepL (DeepL SE) was used for translation and for improving the linguistic quality of selected text passages. ChatGPT (OpenAI) was used to support linguistic revision, the structuring, the refinement of scientific formulations, and the search for relevant scientific literature.

All content generated or revised with the assistance of these tools was reviewed, critically assessed, and, where necessary, revised by me. The selection, interpretation, and presentation of the scientific content were carried out under my own responsibility. I take full responsibility for the content of this dissertation.