

Abstract

This study followed the scientific approach of identifying active sites for electrochemical, corrosive processes on hot dipped galvanized steel and the creation of a material with selective deposition properties that could inhibit the corrosive activity of these weak spots. This study firstly involved high lateral resolution investigations on surface element composition and electrochemical micro probe techniques that identified weak zones on HDG steel substrate. Applying scanning electron microscopy and energy dispersive X-ray spectroscopy it was found that aluminum in HDG alloys (ZnAl 0.5 w.-%) segregates not only towards the zinc/iron and zinc/air interface but especially towards the boundaries of zinc grains. Surface high resolution potential mappings utilizing scanning Kelvin probe – force microscopy showed the electrochemical potential difference of grain boundaries (lower potential) compared to the surrounding grain surfaces: a clear indication for higher corrosive activity of these structures. The application of the micro capillary cell showed that grain boundaries tend to dissolve more easily due to corrosive currents that were measured at lower electrochemical potential (-910 mV) than on single grains (-830 mV). The final corrosion test on a coil coated substrate showed the higher corrosion activity of grain boundaries at the corrosion front. In this test corroded grain boundaries could be observed leading up to 200 μm forward from the main corrosion front into the intact coating/substrate interface. From these findings a model of different corrosion pathways was derived, which suggests that the anodic part reaction quickly propagates forward along the grain boundaries and is escorted by the local cathode. It can be said that on the delaminated substrate surface the main corrosion front can spread out more easily. Based on this model the corrosion propagation would decelerate by inhibiting the grain boundary activity. The second part of this study focused on the design of polymeric material and its selective application to grain boundaries. The anodic dissolution ability of grain boundaries and the preferred release of aluminum cations were thus used for the selective application of corrosion inhibiting materials on these active sites. An initial applicability screening of materials towards grain boundaries showed promising results with autophoresis of water-borne dispersions; among phosphating and surface spontaneous polymerization. Based on these results water-borne block-co-polymer dispersions were synthesized containing adhesion promoting groups such as carboxylic acid, phosphonic acid and triethoxysilane. Application of these polymers exclusively on grain boundaries could be realized with a controlled release of aluminum cations from these weak spots. It was shown that in the pH region of 2.5 to 4.0 grain boundaries start to dissolve and that coagulation of dispersed polymer particles is susceptible towards triple charged aluminum cations. This combination led to selective deposition of polymer particles on grain boundaries. The final proof of concept was provided by a comparison of non-grain boundary treated versus grain boundary treated HDG substrates in a salt spray test. The results showed a significant difference in the condition of the grain boundaries at the corrosion front, where the grain boundaries selectively covered with a specifically designed polymer reduced the anodic dissolution along the grain boundaries by a factor of three to twenty. In conclusion, grain boundaries on HDG steel are highly corrosively active and it was possible to block their corrosive activity by applying polymers only to these weak zones. This new method of selective corrosion protection bears high potential as a promising strategy towards smart and environmentally friendly pretreatment of steel goods.