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Dissertation Outline

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CHAPTER 1. General Introduction

CHAPTER 2. Corrosion behavior of zinc under thin solution films

The corrosion ($1/R_{ct}$) of as-polished zinc is strongly dependent on the solution film thickness (X_f) and the dependency can be divided into three regions. In Region I ($X_f \geq 200 \mu\text{m}$), the solution film comprises two layers, an inner diffusion layer, and an outer convection layer. The reduction of X_f only decreases the thickness of the convection layer. This region corresponds to complete immersion in corrosive media. Therefore, the corrosion rate is independent of X_f , similar to that in bulk solution. However, zinc showed much smaller the corrosion rate compared with carbon steel because the zinc surface is covered by the native zinc oxides film which forms after the surface's polishing. In Region II (X_f : 100–25 μm), the native zinc oxide film would be broken down a tinning of the solution film. The corrosion rate increases with decreasing X_f . In general, the increase in i_{corr} can be explained by the enhancement of oxygen transport through the solution film. Therefore, zinc corrosion is controlled by the cathodic process, that is, oxygen diffusion. In Region III, the corrosion rate decreases with decreasing X_f due to inhibition of the anodic process. In Region III ($X_f < 25 \mu\text{m}$), by further reducing the thickness, the corrosion rate of the as-polished zinc tends to decrease. This trend can be explained by the suppressed anodic reaction. The rate-determining step changes from cathodic (Region II) to anodic control (Region III). (Published)

CHAPTER 3. Formation and characterization of native zinc oxides film

From the results of the corrosion behavior in Region I, it is found that the native zinc oxides film plays a significant role in the atmospheric corrosion of zinc. Therefore, the influence of this native zinc oxides film has been further investigated. Different native oxides, amorphous and crystalline oxides film, are formed on the zinc surface exposed to humidified air in a closed humidity-temperature controlled chamber at two different temperature, 25 and 60 °C, respectively. These oxides films are a mixture of zinc oxide and zinc hydroxide (ZnO/Zn(OH)₂).

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CHAPTER 4. Corrosion behavior of zinc covered with native oxides under thin solution films

In crystalline oxides film, the corrosion rate is dependent on the X_f because the oxygen reduction reaction (ORR) is controlled by O₂ diffusion similar to as-polished zinc. The crystalline oxides film does not suppress the ORR. However, the corrosion rate for the film of the amorphous oxide is independent of the X_f because the ORR is controlled by a charge-transfer step. The ORR is strongly suppressed by amorphous films and reduces the corrosion rate of zinc more than the crystalline oxides film. (Published)

CHAPTER 5. Corrosion behavior of zinc exposed to a marine atmospheric

In the last session, the atmospheric corrosion of zinc in a real marine atmosphere is considered and compared with the as-polished zinc. The rusted zinc obtained by exposure to a natural atmospheric environment for 1, 3, 6, and 12 months. The exposed zinc sample was covered with the insoluble corrosion products, which were

mainly identified as ZnO, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$). The corrosion behavior of rusted zinc is quite different from that of as-polished zinc. The corrosion rate for the exposed zinc is independent of X_f , which means that the corrosion products formed after natural exposure are more protective than the native oxides film. It is evident that the corrosion is under mixed control (charge transfer process and oxygen diffusion) by both the anodic and cathodic reactions and both reactions are inhibited by the corrosion products. In the cathodic reaction, oxygen is not reduced on the corrosion products because simonkolleite, which is one of the main corrosion products, is an insulator. The charge transfer process is strongly suppressed by the insoluble zinc corrosion products, which were identified as $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ and ZnO. (Published)

CHAPTER 6. Conclusions

Conclusions summarizes the significant finding of the present work. The unclear points in the scope of the present study are also discussed and some procedures for further investigation are proposed. Atmospheric corrosion of pure zinc has been successfully studied by EIS and is strongly dependent on solution film thickness. It has been established that in wet atmospheric corrosion, cathodic control still operative, and in humid atmospheric corrosion, anodic control takes over. The influence of zinc oxides film and/or zinc corrosion products was found on the atmospheric corrosion of zinc. These oxides film/zinc corrosion products strongly reduce the corrosion rate because both anodic and cathodic reactions are strongly suppressed by oxides film/zinc corrosion products.