

Drying Effects on Corrosion Properties of Cr(VI) and Cr(III) Treated Electrogalvanized Steel

X. Zhang^(1,2), C. van den Bos⁽²⁾, W.G. Sloof⁽²⁾,
A. Hovestad⁽³⁾, H. Terry⁽¹⁾, J.H.W. de Wit^(1,2)

⁽¹⁾ Netherlands Institute for Metals Research (NIMR)
Rotterdamseweg 137, P.O. Box 5008, 2600 GA Delft, NL
⁽²⁾ Department of Materials Science, Delft University of
Technology, Rotterdamseweg 137, 2628 AL Delft, NL
⁽³⁾ TNO Science and Industrial, P.O. Box 6235, 5600 HE
Eindhoven, NL

Introduction

Despite the good corrosion resistance of chromate conversion coatings, the toxicity of hexavalent chromium involved in this treatment necessitates a search for replacements [1, 2]. As one of potential alternatives to conventional Cr(VI) treatments, trivalent chromium treatment is regarded as commercially acceptable for certain applications in zinc finishing industry [3]. The thermal stability of conversion coatings is interesting because passivated metal parts have to endure heat treatment during the fabrication of assemblies. Previous work shows that dehydration of the chromate coatings can result in loss of the corrosion properties of the coatings [4, 5].

In this paper, we report on studies of the surface structure and electrochemical behaviour of Cr(VI) and Cr(III) treated electro-galvanized steel (EGS) changing with the heating temperature, aimed at understanding the influence of the thermal effect on the corrosion performance of the Cr(VI) and the Cr(III) coatings in a solution containing chloride.

Experimental

Electro-galvanized steel (~ 13 µm thick zinc coating) was activated in 0.25% HNO₃ solution for 30 seconds and rinsed in deionised water. For the purpose of doing surface analysis, pure zinc sheets (0.5 mm thick) were polished to 1 µm and ultrasonically cleaned in acetone and alcohol for 2 minutes, respectively. Cr(VI) treatment was carried out on the EGS in a bath containing 200 g/L Na₂Cr₂O₇ + 10 g/L H₂SO₄ (pH 1.2) for different dipping times. The chromate-coated samples were rinsed in deionised water and heated in an oven at 60, 110 and 210°C for 30 minutes. The Cr(III) treatment was carried out in a commercial bath (Permapass 3K, pH 1.8), which contains fluoride and sulfate as accelerators. The Cr(III) treated specimens were heated in an oven at 70, 110 and 210°C for 30 minutes.

The morphology and compositions of treated samples were analyzed using SEM, AES and XPS. The corrosion behaviour of these specimens in NaCl solution was investigated using d.c. polarization and a.c. impedance measurements.

Results and discussions

The Cr(VI) treated EGS showed microcracks in the coatings. The microcracks became wider when the heating temperature was higher. AES depth profiles show that the outmost layer of the Cr(VI) coating comprises mainly chromium oxides/hydroxides. Zinc oxide in the top layer is less than 4%. Zinc oxide is detected mainly at the interface between the chromium oxides/hydroxides and the zinc metal substrate. The Cr(III) coatings contain a mixture of chromium oxides and zinc oxide through the layer, and the

content of zinc oxide is more than chromium oxides. XPS analysis results show that by increasing the temperature from 60 to 110 and 210°C, the ratio of Cr(VI) to total chromium in the Cr(VI) coating decreased from 35% to 32% and 12%, respectively.

Polarization measurements show that the corrosion current density of the EGS is inhibited by both Cr(VI) and Cr(III) treatments. Increasing the heating temperature results in an increase of the corrosion current for the Cr(VI) and the Cr(III) coatings. EIS results show that the magnitude of the impedance decreases with the heating temperature.

Conclusions

Cr(VI) and Cr(III) coatings on EGS can act as barrier layers and cathodically inhibit zinc corrosion in aqueous solution. With increasing of the heat temperature, the corrosion resistance of the Cr(III) treated EGS decreases. For the Cr(VI) treated EGS, the heat temperature affects not only the coating morphology, but also changes the chromium oxidation states in the coating. All of the Cr(VI) coatings investigated in this study showed microcracks in the layer. The width of these cracks increased with the temperature. The coatings dried at 60°C showed passivity. Drying at a moderate temperature (110°C) the chromate coatings lost passivity and drying at higher temperatures (210°C) degraded the chromate coatings by widening the cracks and reducing the mobility of the soluble Cr(VI) species. The thermal reduction of Cr(VI) in the layer is also responsible for the decrease of corrosion resistance.

Acknowledgement

This research was supported by the Dutch Ministry of Economic Affairs (Innovation-directed Research Program for Environmental Technology/Heavy Metals, project IZW98102).

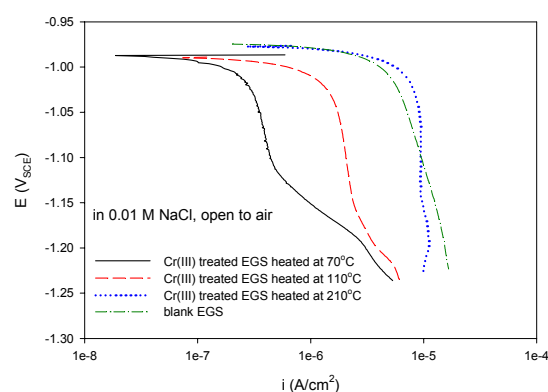


Fig. 1 Cathodic polarization curves measured in 0.01 M NaCl solution for Cr(III) treated EG steel heated at different temperatures and for untreated EG steel.

References

1. R. L. Twite and G. P. Bierwagen, *Prog. Org. Coat.*, **33** (1998) 91.
2. M. W. Kendig and R. G. Buchheit, *Corrosion*, **59** (2003) 379.
3. P. C. Wynn and C. V. Bishop, *Trans IMF*, **79** (2001) B27.
4. V. Laget, C. S. Jeffcoate, H. S. Isaacs, and R. G. Buchheit, *J. Electrochem. Soc.*, **150** (2003) B425.
5. X. Zhang, S. Bohm, A. J. Bosch, E. R. M. van Westing, and J. H. W. de Wit, *Mat. Corros.*, **55** (2004) 501.