Passivation of Electrogalvanized Steel with Conversion Coatings in CR VI-FREE solutions

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Introduction

Zinc is commonly used as anti-corrosive coating because of its low cost and good performance when compared to other protective coatings. However, zinc protection is not very satisfactory when exposed to harsh conditions. A way of improving zinc protective properties is to passivate its surface by means of surface treatments in order to make it less reactive in aggressive environments. Passivation might be carried out by conversion coating layers in presence of hexavalent chromium ions. This treatment has been used for many decades as a highly effective protection against fast zinc corrosion. However, its toxic and carcinogenic effects, besides the high costs involved in wastewater treatment have recommended research in search for replacement treatments with similar protective properties. Several studies have been carried out to replace this kind of layers[1,2]. Among the most investigated passivating groups are the analogous to the metal oxyanions chromate (molybdates, vanadates, tungstates and permanganates), silicates[3] and silanes[4]. Currently, passivation by rare earths has also been studied[5]. This work aims to study hexavalent chromium free surface treatments and their effects on the corrosion resistance of electrogalvanized steel.

Experimental

Carbon steel plates were used as substrate for zinc electrodepositon. The surfaces were pickled in HCl 50% v/v, degreased and activated for 2 min in 5% v/v ammonium bifluoride solution. Zinc was electrodeposited from an alkaline zinc bath cyanide-free solution. The zinc layer thickness was estimated by scanning electron microscopy (SEM) of cross-section samples and it was in the range from 11 to 13 μm.

After zinc electrodeposition, the surface was activated in 1% v/v HNO_3 solution. The zinc eletrodeposited plates were then passivated by immersion in different solutions at room temperature during 1 minute. The estimated thickness of the conversion coatings was in the 100-500 nm range. The main components of the passivation solutions tested in the present study are shown in Table 1:

Table 1: Solutions used for passivation of zinc eletrodeposited steel samples.

Passivation	Passivation solution
1	Potassium silicate and sodium nitrate.
2	Treatment 1 followed by immersion in 2-butyne-1,4-diol propoxylate
3	Hexavalent chromium.
4	Treatment 2 followed by coating with an inorganic sealant.

Evaluation of the corrosion resistance of zinc eletrodeposited steel samples after passivation was carried out by anodic polarization after 30 minutes of immersion in the test solution (0.1 M NaCl). Electrochemical impedance spectroscopy (EIS) tests were also carried out after 6 days of immersion in the test medium. The surface of the samples with the various passivation treatments that had been immersion for 30 minutes in 0.1 M NaCl and then polarized anodically was analyzed by Scanning Electron Microscopy - Field Emission Gun (SEM-FEG).

Results and Discussion

The anodic polarization curves of all types of passivation treatments tested after 30 min. immersion are shown in Figure 1.
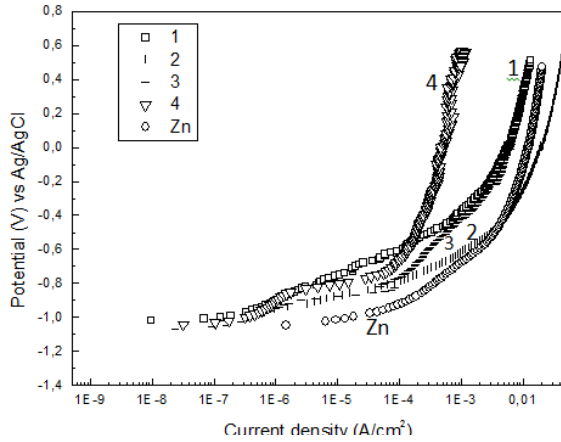

Figure 1: Anodic polarization curves obtained after 30 minutes of immersion in 0.1 M NaCl solution.

Passivation 4 resulted in polarization of the anodic reaction, as indicated in Figure 1. This might be related to the use of inorganic coating that produced a surface with higher corrosion resistance than that of the passivation with hexavalent chromium.
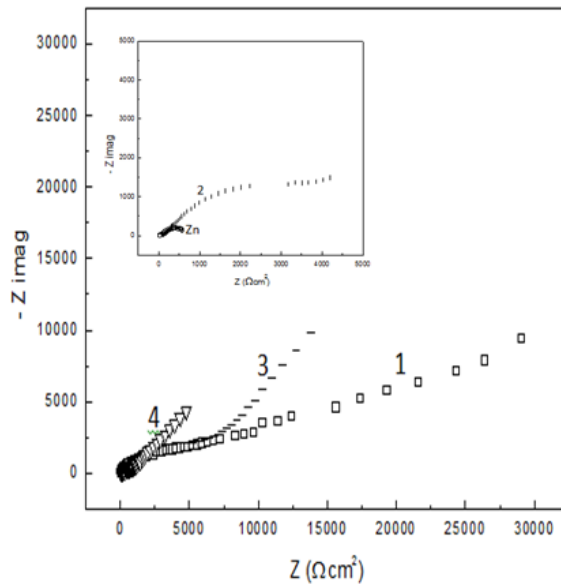
Figure 2: Nyquist diagrams of the samples after 6 days of immersion in 0.1 M NaCl solution.

Electrochemical impedance spectroscopy (EIS) results for all treatments after 6 days of immersion in the test solution are shown in Figure 2 as Nyquist diagrams. The impedance results showed very low corrosion resistance associated to passivation 2, corroborating the polarization results that indicated a deleterious effect of the 2-butyne-1,4-diol propoxylate addition to the passivating bath on the protection of the zinc layer. On the other hand, the surface film resulting from passivation 1 showed the

highest impedances among the tested treatments, after 6 days of immersion, even superior to that related to passivation 3 and 4. This result suggests the degradation of the inorganic sealant on the surface with this last treatment, with time of immersion. This result is supported by the micrographs shown in Figure 3 and the Nyquist diagrams of Figure 2. The results also suggested that passivation 1 might be a potential treatment for replacement of the hexavalent chromium based type.
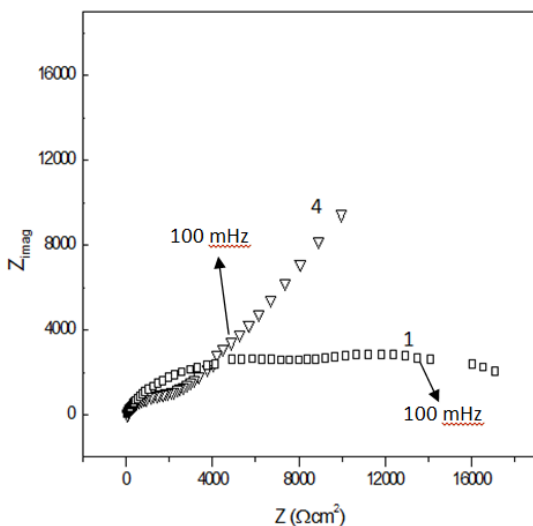

Figure 3: Nyquist diagrams for surface treatment 1 and 4 after 2 hous in 1 M NaCl solution.

Figure 4 shows the SEM-FEG micrographs of the various tested samples after anodic polarization curves. The micrographs show that after 30 minutes of immersion and anodic polarization curves, the surfaces with passivation 1 and 4 presented higher pitting corrosion resistance, superior to that with Cr-VI.

The low effective protection of the film formed in presence of 2-butyne-1,4-diol propoxylate, without sealant corroborating the electrochemical results. The SEM micrographs indicated the preferential concentration of Si at some particles on the surface, as indicated in Figure 4 (2 a)), comparatively to the surface film, and spherical pits that initiate around small particles, but spread out from them. This result supported the harmful effect of the 2-butyne-1,4-diol propoxylate on the passivating treatment decreasing the pitting resistance. The sealant acts as by a barrier mechanism effect impairing the access of the corrosive species from the electrolyte to the substrate. The deterioration of the sealant layer must have been influenced by the surface pre-treatment prior to its application.
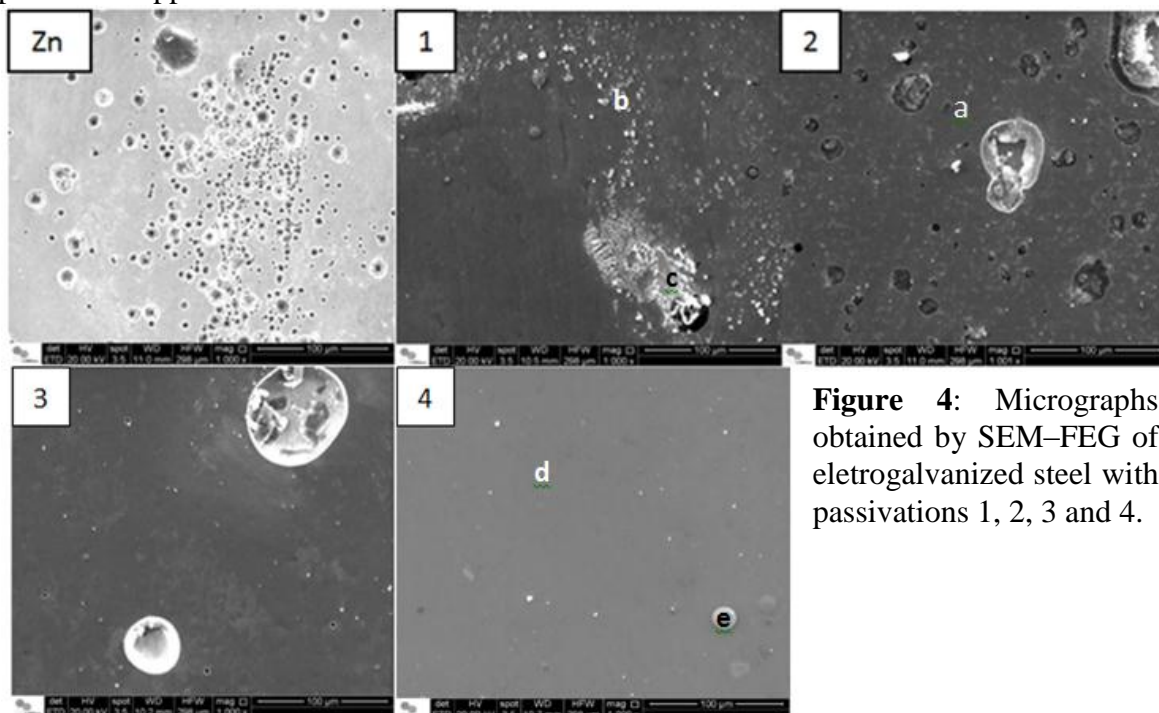

Figure 4: Micrographs obtained by SEM–FEG of eletrogalvanized steel with passivations 1, 2, 3 and 4.

Conclusions

The results of polarization curves and SEM–FEG obtained after 30 minutes of immersion in NaCl solution, showed that the addition of 2-butyne-1,4-diol propoxylate to the silicate conversion bath had a deleterious effect on the passivation of electrogalvanized steel. On the other hand, coating this surface with an inorganic sealant increased the corrosion resistance of the surface. Passivation with silicate and nitrate provided the most protective surface film for long immersion periods (6 days in 0.1 M NaCl solution) and suggested that this treatment could replace the hexavalent chromium based conversion layers.

Acknowledgements

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