

Study of Zirconium Addition on CR VI-FREE Passivating Layers Applied on Zinc Coated Steel

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Introduction

Zinc coated steel are widely used because of zinc corrosion protection properties. However, in aggressive conditions such as temperatures above 110 °C and atmospheres of high humidity, the zinc protective layer is rapidly attacked and a surface treatment is necessary a treatment to increase the zinc corrosion resistance. Conversion layers have been applied to the zinc layer in order to increase the zinc protective properties^{1,2}. The conversion coating treatment which is highly effective for the zinc layer protection against fast corrosion is that with hexavalent chromium ions. However, due to the toxic and carcinogenic effects associated to this treatment, it has been increasingly prohibited. Alternatives, such as the use of zirconium have been studied as a promising component of conversion layers³⁻⁵. In the present study the effect of zirconium addition to Cr VI free surface treatments of electrogalvanized steel has been investigated.

Experimental

Carbon steel plates were used as substrate for zinc electrodeposition. Their surfaces were pickled in HCl 50% v/v, degreased and activated for 2 min in 5% v/v ammonium bifluoride. Following, zinc was electrodeposited from a cyanide-free alkaline zinc bath. After zinc electrodeposition, activation was performed in 1% v/v HNO₃ followed by passivation by dipping the electrogalvanized samples for 1 minute in the passivation baths shown in Table 1 at room temperature.

Table 1: Passivation baths used for surface treatments of electrogalvanized steel.

Treatment	Bath composition
1	Potassium silicate and sodium nitrate.
2	Potassium silicate, sodium nitrate and diammonium dithioglycolate.
3	Potassium silicate, sodium nitrate and zirconium, pH 2, followed by coating with an inorganic sealant.
4	Hexavalent chromium.
5	Potassium silicate, sodium nitrate and zirconium, pH 2.

Anodic polarization curves were obtained after 30 minutes of immersion in the test solution (0.1 M NaCl). Electrochemical impedance spectroscopy (EIS) tests were carried out after 6 days of immersion in the test medium. Scanning Electron Microscopy – Field Emission Gun – Quanta (SEM-FEG) was used to examine the passivated electrogalvanized steel surfaces that were immersed for 30 minutes in 0.1 M NaCl solution and then polarized.

Results and Discussion

The zinc layer thickness was estimated by SEM-FEG of cross-section samples being in the range from 11 to 13 µm. The anodic polarization curves for all types of passivation treatments studied are shown in Figure 1.

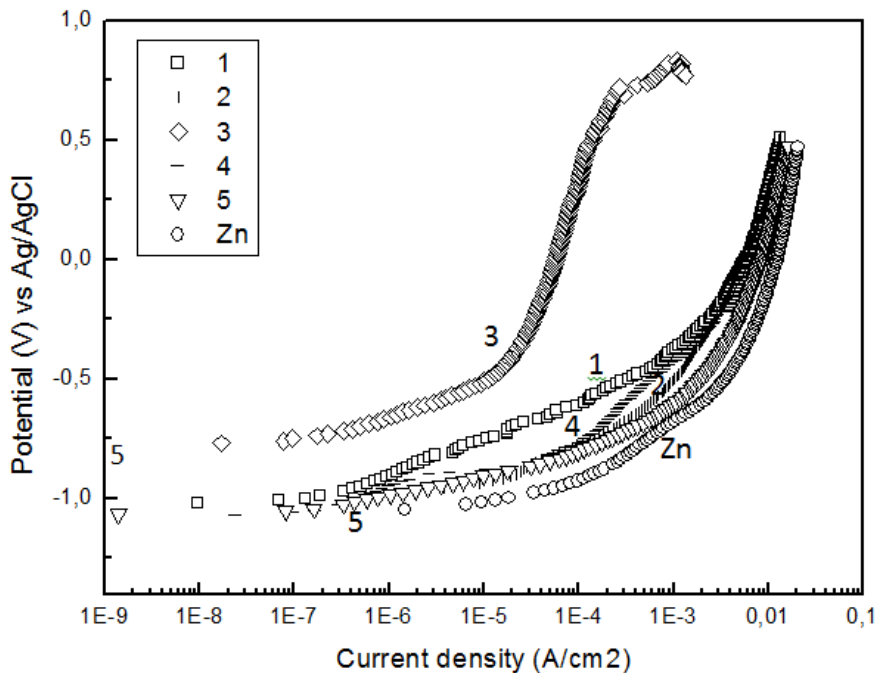


Figure 1: Anodic polarization curves after 30 min. of immersion in NaCl 0.1 M.

As can be seen in Figure 1, the lowest corrosion currents were associated to treatment 3, most likely due to the use of an inorganic sealant on the surface protection. A comparison of treatments without sealant showed lower corrosion

currents associated to treatment 1 comparatively to that with hexavalent chromium ions (treatment 4), suggesting that this could be considered for replacement of the last type. Electrochemical impedance spectroscopy (EIS) results obtained for all treatments after 6 days of immersion in the chloride solution are shown in Figure 2 as Nyquist diagrams.

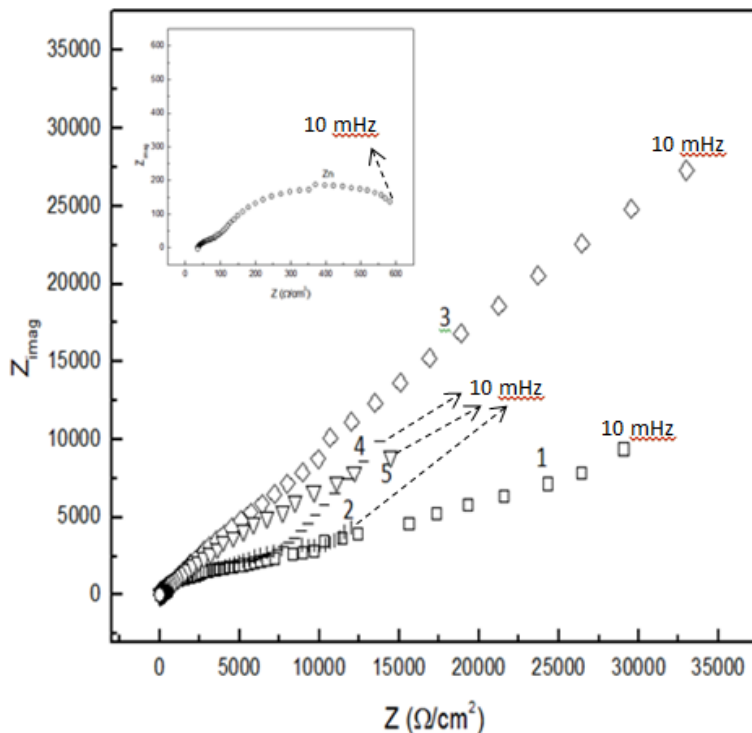


Figure 2. Nyquist diagrams for the tested surfaces at 6 days of immersion.

The EIS data supported the polarization results, showing the highest impedances associated to treatment 3. These results also indicated a deleterious effect of the diammonium dithioglykolate resulting in lower impedances comparatively to the treatment in a similar solution without it.

Figure 3 shows micrographs obtained by SEM-FEG of samples with all surface treatments studied after anodic polarization. A comparison of the Si content on the regions indicated as m and l showed lower Si contents on the surface of the samples exposed to treatment 2. This treatment was also associated to high pits density comparatively to treatment 1. This suggests a competition of silicate and diammonium dithioglykolate for the zinc substrate, with silicate acting as a more

effective inhibitor than the diammonium dithioglykolate. The micrographs also suggest that the treatments 1, 3 and 5 inhibited the pit formation on zinc coated steel.

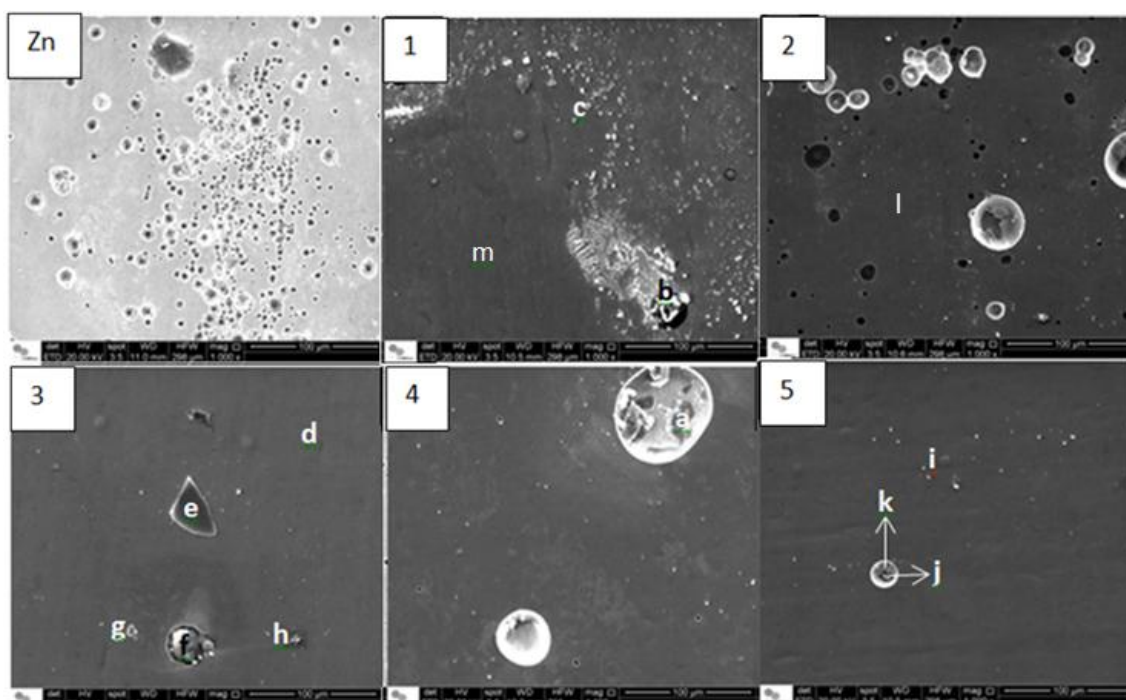


Figure 3: SEM micrographs of samples immersed for 30 minutes in 0.1 M NaCl solution followed by anodic polarization. The inserted numbers indicate the passivation treatment whereas the letters indicate the points analysed by EDS.

For the passivation with hexavalent chromium, the pits density decreased but the pits were larger comparatively to that associated to the other surface treatments. Chromium was detected on point a, which corresponds to a pit. A comparison of treatments 1 and 5 indicates that the addition of zirconium to the passivation produced a more uniform surface, with similar impedances to that of the passive film with hexavalente chromium. Small and shallow pits were associated to this surface suggesting a beneficial effect of zirconium in the passivating bath.

Conclusions

The addition of zirconium into passivation baths had a beneficial effect on the corrosion resistance of galvanized steel, reducing its susceptibility to pitting and increasing the surface homogeneity. The use of an inorganic sealant on this surface increased further its corrosion resistance being superior to that related to the tested Cr VI passivation.

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