Electrochemical characterization of passivated electrogalvanized steel

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Introduction

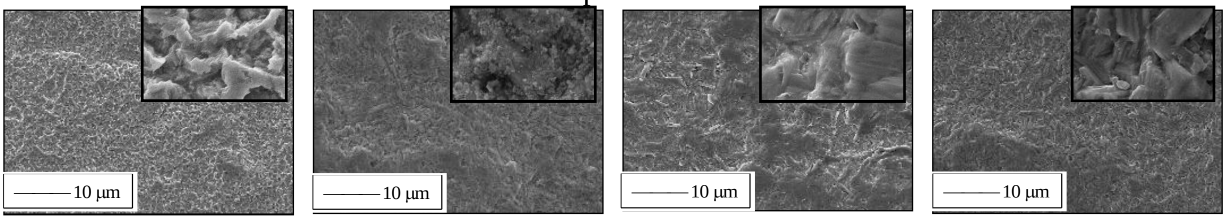
The chromate conversion treatment is widely used, but it requires highly toxic chromic acid solutions, with consequent effluent disposal and ecological problems [1-5]. The removal of these toxic chemicals is considered a priority within European Union. In this work, the corrosion resistance behavior of three alternative pretreatments applied on electrogalvanized steel was investigated by EIS. Their results were compared with those obtained for traditional Cr^{6+}-based pretreatment exposed to the same conditions. The experiments were carried out in sulfate solution, pH 10, at 25 °C. From the analyses and interpretation of the attained data could be inferred that the alternative coatings systems exhibited discrete protective properties in aerated alkaline sulfate solution. The nitro-cobalt chemical conversion treatment showed protective properties like the traditional Cr^{6+}-based one, while the Cr^{3+}-based pretreatment displayed a very poor anticorrosive performance, and the phosphate one initially provided good protective action but this decreased as the time elapsed.

Experimental

Electrogalvanized steel samples industrially produced with 10 μm of thickness and covered with the following commercial conversion treatments: (**A**) Cr^{+3} chromate; (**B**) nitro-cobalt chemical conversion; (**C**) phosphate; and (**D**) traditional Cr^{6+} chromate, were investigated.
Coatings morphology was observed by SEM using a LEICA S440 microscopic.
EIS measurements were performed in the frequency range between (10^{-2} a 10^{5}) Hz using a Solartron 1260 FRA coupled to a Solartron 1286 electrochemical interface, and a sinusoidal voltage signal of 3 mV. The corrosion behavior was analyzed till the appearance of white corrosion products on the samples surface [6]. All measurements were performed at 25 °C in 0.3 M Na_2SO_4 solution, pH 10 (adjusted by NaOH solution), in which the zinc dissolution rate is very slow [7]. The electrochemical cell consisted of a PMMA cylindrical electrolyte holder attached to the coated surface filled with the test solution. The exposed area was 7.07 cm^2. Coated metal was the working electrode. A reference electrode SCE and a Pt counter electrode were employed.

Results and Discussion

Coatings surface morphology was observed by SEM at 2.000X and 10.000 x enlargement, Fig. 1. **A** treatment presented a less uniform structure formed by smaller nodular grains. At lower magnifications, the **B** treatment exhibited small spherical shaped particles distributed over the surface, which have a strong tendency to agglomerate forming filaments. The surface morphology of **C** and **D** treatments was very similar and exhibited a plate-like structure. The **D** treatment showed a more uniform and compact structure.



(a) **A** treatment (b) **B** treatment (c) **C** treatment (d) **D** treatment

Fig. 1: SEM micrographs of the Zinc covered with different conversion treatments.

Figure 2(a) shows the Bode plot for **A** treatment. It was observed, at 0.02 Hz, tended to increase slightly as the time elapsed up to reach values near to 2.10^3 Ω.cm^2. After 24 h of immersion, at medium frequencies was observed a decrease of |Z|, that is, an increase of the capacitance value. At high frequencies, the |Z| values are related to the corrosion resistance of the conversion coating and, as they did not change during the immersion period, it suggests that the surface remained unchanged during this period. In Figure 2(b), it was observed a time constant with a maximum phase angle value of 58°, and also that, at 0.02 Hz, the phase angle curve slope suggests the appearance of a second time constant. After 2 h of immersion and, at medium frequencies, it is observed a small variation of this time constant and its disappearance after 24h of immersion. A possible justification of such behavior is based on the assumption that the conversion coating is not compact. So, initially, the surface corrosion protection took place through the gathering of corrosion products within and/or at the bottom of the coating pores, but as the time elapsed that protection is lost because the products diffused towards the bulk of the solution.

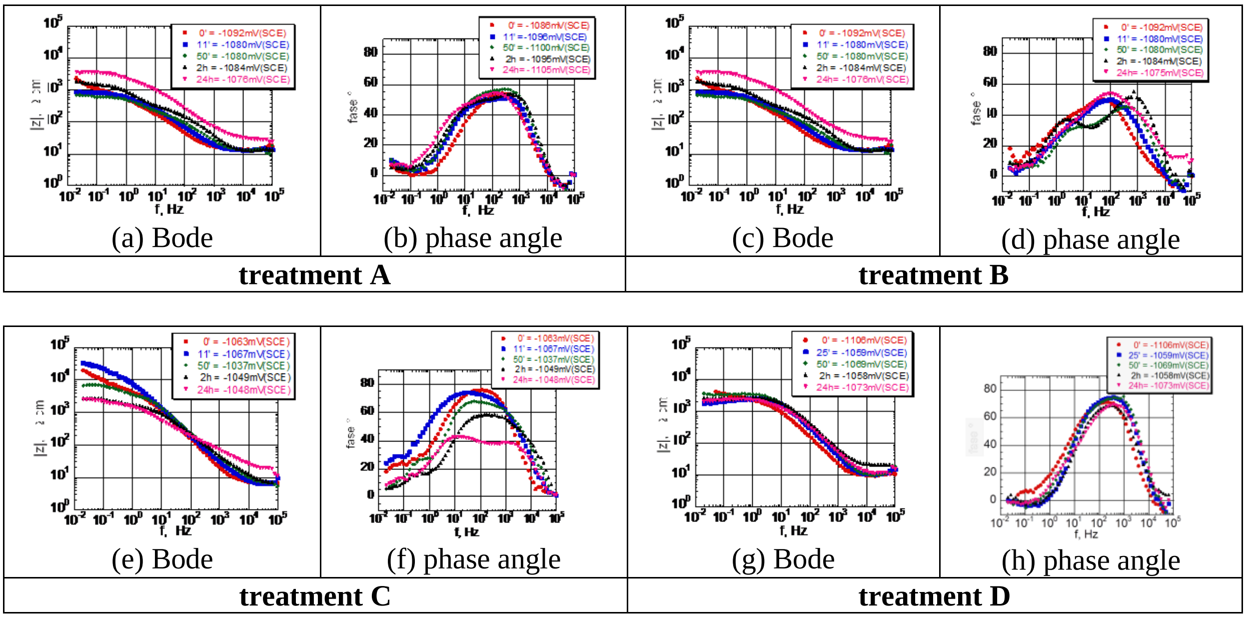
Figure 2(c) shows the Bode plot for the **B** treatment. At 0.02 Hz was observed an oscillating behavior during the immersion time. It was attributed to the existence of a corrosion reaction at the interface, in agreement with the variation of the potential values. At high frequency was observed an increase of the |Z| value after 24 h of immersion, which suggests a compaction of the corrosion products within and/or at the bottom of the coating pores causing an inhibition of the corrosion process. In Figure 2(d) only one time constant associated to the presence of the treatment film and with a maximum phase angle of 55° was observed but, after 50 min, a second time constant appeared indicating that the corrosion of the substrate surface had started. After 24 h, the second time constant disappeared, possibly due to the coatings defects were blocked by the corrosion products developed and, consequently, the corrosion process was inhibited.

Figure 2(e) shows the Bode plot for **C** treatment**.** At 0.02 Hz, an oscillating behavior during the first hour was detected, being the initial |Z| value equal to 2.10^4 Ω.cm^2. After the first hour, the |Z| values tended to decrease as a function of immersion time. At high frequency, an increase of |Z| with the immersion time was observed, which suggests an improvement on the coating protective properties, but this improvement was not enough to prevent the corrosion of the substrate during larger immersion periods. This type of behavior can be explained assuming that the developed corrosion products were able to block the coatings defects sufficiently as to inhibit, at least partially and temporarily, the occurrence of the substrate corrosion reactions. Figure 2(f) shows phase angle shift as a function of immersion time in the test solution for the **C** treatment. For the first 2 h immersion at least two time constants were well defined. The high frequency one was associated to the presence of the treatment film, while the observed at the low frequency range was associated to the zinc corrosion reaction. After 24 h, a third time constant appeared at medium frequencies and this was interpreted as an evidence of the corrosion products contribution to the overall system impedance.

Figure 2(g) shows the Bode plot for the **D** treatment. At 0.02 Hz a slightly oscillating behavior of the |Z|, with an initial value of 5.10^3 Ω.cm^2, was observed. At high frequencies can be noted that the conversion coating initially offers a corrosion protection due to the gathering of corrosion products within and/or at the bottom of the coating pores, but after 24 h of immersion the |Z| value went back to its initial value. This means that after the initial protection offered by the corrosion products, a more significant degradation of the conversion layer took place. Changes happening in the conversion layer have highly detrimental effects on the corrosion behavior of the coated steel.

Figure 2(h) shows phase angle shift as a function of immersion time in the test solution for the **D** treatment. It can be seen that the time constant at low frequencies, and present just after immersion (t = 0), disappeared after 25 min of immersion and it was substituted by an inductive loop. At medium frequencies there was a phase angle maximum of 75°. A second time constant did not appear which means that the slight modifications occurred in the conversion layer did not affect the behavior of the total coating.

A qualitative analysis of the EIS data shows that the **C** and **A** treatments suffered degradation and corrosion at the metal/conversion layer interface during the exposure to the alkaline solution, while **D** and **B** treatments remained more or less unchanged and showed the best performance. Thus, the deterioration with the conventional Cr^{6+}-based treatment was lower than that of the tested alternative conversion treatments; probably due to its layer was structurally and morphologically more uniform and compact than others ones.



(a) Bode (b) phase angle (c) Bode (d) phase angle

treatment A **treatment B**

(e) Bode (f) phase angle (g) Bode (h) phase angle

treatment C **treatment D**

Fig. 2. Bode and phase angle plots as a function of immersion time in aerated 0.3 M Na_2SO_4.

Conclusions

The development of the present experimental study allows the following main conclusions to be drawn: (a) all treatments presented white corrosion products after 24 h of immersion in 0.3 M Na_2SO_4 solution at pH 10; (b) the EIS data showed the different coatings corrosion behavior in the initial stage of the immersion, but after 2 h of immersion was difficult to observe such difference, probably due to the formation of corrosion products, not visible by the naked eye; (c) EIS data demonstrated that the **D** treatment showed good corrosion protection, which was comparable to the **B** treatment, and that the **A** treatment provided the poorer protective properties; (d) initially, the **C** treatment showed good anticorrosive protection but this decreased as the exposure time elapsed; (e) the more uniform and compact coating presented the best corrosion behavior.

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