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Electrochemical Behaviour of Electrogalvanized Steel with a Conversion Treatment at Room Temperature

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Conversion treatments applied on electrogalvanized steel are largely used for corrosion protection. Cr^{3+} based conversion treatment has been established as an alternative to Cr^{6+} treatments. However, commercially available baths operate at temperatures around 60 °C and use high concentrations of Cr^{3+} salts. In order to attend the world market demand for processes with low energy consumption and Green Technologies, a Cr^{3+} treatment has been developed with much lower contents of Cr^{3+} salts, about 80% lower, which operates at room temperature. The corrosion resistance of surface treated electrogalvanized steel in baths with two different concentrations of Cr^{3+} ions was evaluated by electrochemical impedance spectroscopy in chloride solution. The results showed that the surface treatment with low Cr^{3+}concentration and carried out at room temperature, leads to better corrosion resistance in comparison to the commercial type, and it might be considered as a potential replacement for chromating treatments that have been increasingly banished from use.

Introduction

Hexavalent chromium conversion treatments are still used in some countries. European regulations, however, tend to restrict their use and the companies are developing new surface treatments in order to attend the new demands (1-3). Consequently, the development of new conditions for the conversion treatment of zinc, are necessary (4,5).

Several alternative conversion treatments have been proposed that used "metal oxyanions" analogous to the chromates, such as, molybdates, vanadates, tungstates and permanganates (4,5). Among these compounds, molybdates were further investigated due to their known ability to reduce the susceptibility of stainless steels to pitting corrosion (6). Recently, many other alternative coatings based on rare earth salts were developed (7-11). However, the methods of preparation and the corrosion resistance associated to these coatings are not clear and their practical use is still uncertain.

Despite the constant search for chromium free alternative baths, the use of electrolytes containing trivalent chromium salts still stands out as the best option to hexavalent chromium treatments. Consequently, trivalent chromium based treatments have been continuously improved (5). From the initial studies, increasingly interest arose in the scientific world to improve the properties of trivalent chromium conversion coatings, once these are non-toxic to humans or to the environment and produces a barrier layer

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that protects effectively against corrosion (12-13). Despite the improvements in the conversion coating treatments, the trivalent chromium content in commercially available chromate baths is high and, additionally, they operate at temperatures of approximately 60 °C. In the present work, new surface treatments based on trivalent chromium ions and carried out at room temperature, were used and their effect on the corrosion resistance of electrogalvanized steels was evaluated by electrochemical impedance spectroscopy (EIS). The results were compared to that of a commercially available trivalent chromating treatment.

Experimental Methods

Materials and samples preparation

AISI 1010 steel sheets (65 x 100 x 1 mm) were electrogalvanized using a cyanide-free alkaline bath containing Zn^{2+} 12.5 g/L, KOH 170 g/L, Na_2CO_3 80 g/L and commercial addition agents (Temperature (22 ± 3) ºC and cathodic current density 2 $A.dm^{-2}$. The average zinc thickness is 10 µm. After the zinc deposition step, each sample was exposed to either one of the conversion treatments shown in Table I. To reactivate the surface, the electrogalvanized samples were etched by immersion in an acid solutions (HNO_3, pH 1 for 20 s). Finally, the samples were rinsed with deionized water in triple cascade and then dried at 80°C for 15 minutes.

It is important to know that treatment B was a reformulation from treatment A which allowed passivate electrogalvanized steel at room temperature with a lower chromium content.

TABLE I. Operating conditions of conversion treatment used

Parameters	Conversion treatment A: trivalent chromium based	Conversion treatment B: low content trivalent chromium based
bath concentration	12,5 % v/v	10 % v/v
bath temperature	60 °C	25 °C
pH	1.8	1.8
immersion time	60 s	60 s
agitation	mechanical	mechanical

Surface analysis

A Philips XL 30 Scanning electron microscope, equipped with an EDAX energy dispersive X-ray spectrometer (Si detector and 20 keV energy), was used for surface characterization.

Electrochemical measurements

In this work, a three-electrode cell system was used with a Pt-Rh mesh and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. The surface treated electrogalvanized steel samples were used as working electrode. The electrochemical behavior of the surface treated samples was monitored with time of exposure to the NaCl 0.5 M solution by EIS measurements, using a Gamry PCI4/300 potentiostat/galvanostat, controlled by the Gamry Echem Analyst software. The EIS data

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were obtained using a sinusoidal perturbation signal of 10 mV a.c. amplitude, within a frequency range from 10^{-2} to 10^{4} Hz, and the acquisition rate corresponded to 10 points/decade. The evolution of the corrosion resistance was analyzed until white corrosion products could be seen on the surface. All the measurements were performed at (22 ± 3) °C with the electrochemical cell inside a Faraday cage to eliminate magnetic external interferences. The stationary condition was checked by measuring the corrosion potential after all the EIS tests to confirm that potential variation from the initial value was not greater than ± 5 mV.

Results

Conversion layers obtained from treatments A and B are shown in Figures 1 (a) and 1 (b), respectively; as it shows, they are compact and present no cracks. The layers presented a shiny and iridescent green color aspect.

Semi-quantitative compositional analysis by EDS of the surface treated samples, indicated a concentration of approximately 2.1 wt % of chromium, from treatment A, and 1.5 wt % from treatment B. It is important to note that EDS analysis from electroplated layers surface treated in hexavalent chromium based baths, showed chromium concentrations around 10.1 wt % of chromium (12, 13).

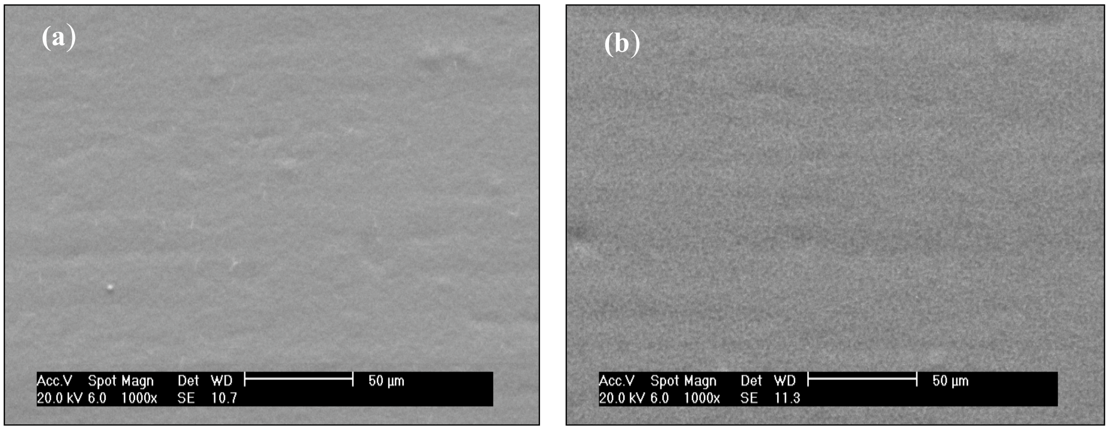

Figure 1: SEM images from electrogalvanized steel after surface treatment corresponding to: (a) conversion coating treatment A, Cr III based bath and (b) conversion coating treatment B, with low Cr III concentration.

Figures 2 and 3 show the EIS results as Bode diagrams for the surface treated electrogalvanized steel samples after treatments A and B, respectively.

A comparison of Figures 2 and 3 shows much lower stability of the surface with treatment A comparatively to treatment B. The corrosion resistance of the first largely varied since the first days of immersion. A large impedance decrease was seen from 28 to 44 days of immersion, and at this last period, white corrosion products were seen on the surface and the EIS monitoring was finished. The surface with treatment B, however, showed good stability from the first hours up to 39 days of test. White corrosion products were seen on this type of surface only after 62 days of immersion. After this period of time, the Bode phase angles diagrams also shows two time constants, indicating coating degradation.

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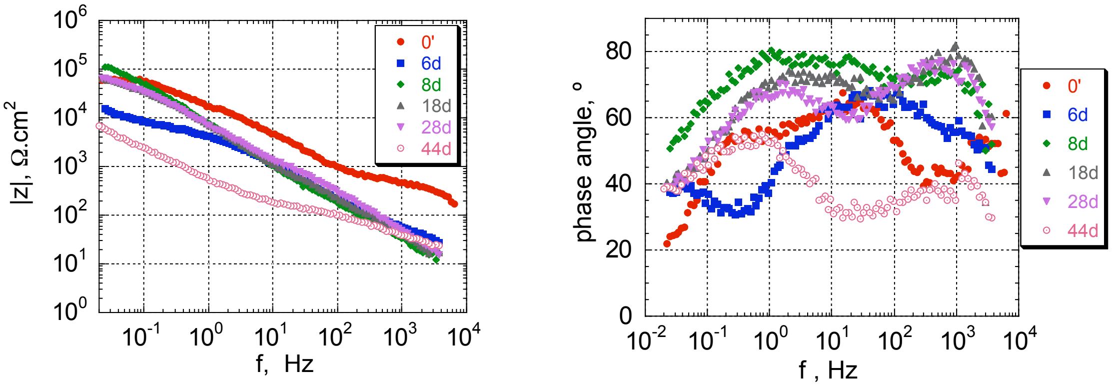

Figure 2: Evolution of Bode diagrams for electrogalvanized steel with conversion coating treatment A, as a function of time of immersion in NaCl 0.5 M: (a) |Z| vs. log f and (b) phase angle vs. log f.

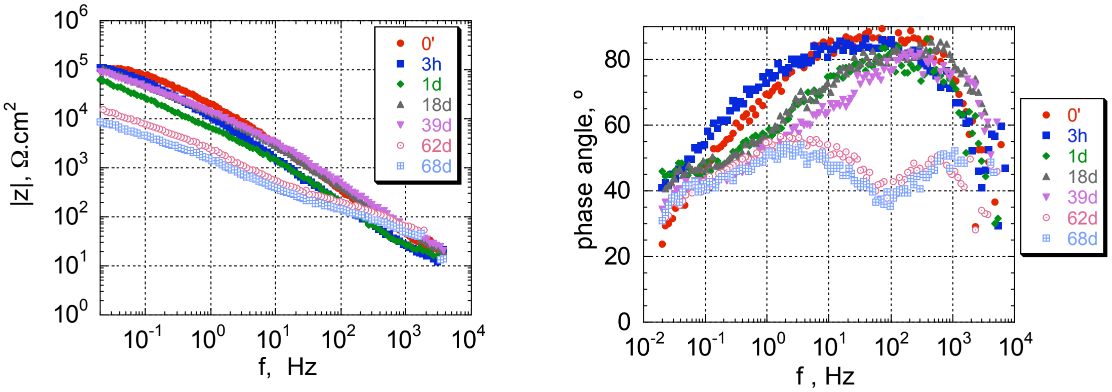

Figure 3: Evolution of Bode diagrams for electrogalvanized steel with conversion coating treatment B (low Cr III concentration), as a function of time of immersion in NaCl 0.5 M: (a) |Z| vs. log f and (b) phase angle vs. log f.

As mentioned in the introduction, trivalent chromium is benefic for the corrosion resistance of conversion coating. Moreover, Cr^{3+} has been the best substitute to hexavalent chromium. However, treatment with a low content of chromium that allows application at room temperature is extremely interesting economically and environmentally.

These results show that the treatment B which is the new treatment proposed in the present study, with low trivalent chromium content and that is carried out at room temperature, was associated to a more corrosion resistant conversion layer suggesting that it could be used as a potential replacement for available commercial treatments available.

Conclusion

The results of the present work led to the conclusion that the conversion coating treatment with low trivalent chromium concentration and carried out at room temperature showed a greater protection against corrosion of the electrogalvanized steel in comparison to the commercial type, and it might be considered as a potential replacement for chromating treatments that have been increasingly banished from use. These results pointed the technological and economic advantages of this development.

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