A Combination of Cerium and Niobium Treatments for Corrosion Protection of Electrogalvanized Steel

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Introduction

Conversion coatings with hexavalent chromium are one of the most effective treatments for passivation of electrogalvanized steels used in the automotive industry [1]. However, the processes that lead to this type of coatings also generate toxic residues such as hexavalent chromium ions (Cr^{6+}). Besides, the oxidant character of these ions might cause oxidation of cells, and, carcinoma. The combination of carcinogenic properties and generation of toxic residues have stimulated researches in search for replacement of the increasingly banished chromating treatments [2]. The researches carried out have involved treatments with many types of elements, such as trivalent chromium, molybdenum, tungsten, vanadium, manganese, ruthenium and niobium [3,4]. Niobium is one of the few non-toxic elements. It is usually added into steels to improve their corrosion resistance. Brazil retains one of the largest reserves of niobium ores in the world. Consequently, niobium has been associated to corrosion protection, either as an alloying element or as combined in surface treatments. Ammonium niobium oxalate (ANO) is a niobium precursor and byproduct of the niobium production metallurgy industry. It has been used in research studies for corrosion protection of phosphated steels [5]. The aim of this study is to investigate the effect of combining two types of surface treatments, using Ce^{3+} and ANO, on the corrosion protection of electrogalvanized steel.

Experimental

The substrate used for passivation treatments was electrogalvanized steel with 100 mm x 150 mm x 10 mm. The electrogalvanized samples were treated by sequential immersion in solutions of different composition, firstly one with cerium ions, then a solution with hydrogen peroxide, and finally in a solution with ANO at 30 ^{o}C. The samples were dried at 100 ^{o}C for 10 minutes. The corrosion resistance of the treated samples was evaluated by electrochemical impedance spectroscopy (EIS) monitoring as a function of immersion time, for 7 days, in a solution of 0.1 M NaCl. The EIS data were obtained at the open circuit potential using a *Gamry EIS 300* coupled to a potentiostat and controlled by the *Echem Analyser 135* software. The EIS tests were carried out over a frequency range from 10 kHz to 10 mHz, with a perturbation signal of 10 mV and a scan rate of 10 points per decade. A three-electrode experimental setup was adopted with an Ag/AgCl reference electrode and a platinum wire as auxiliary electrode. A 1 cm^2 area was exposed to the electrolyte. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM - EDX) was used for evaluation of the surface treated samples.

Results

Fig. 1 (a) and (b) shows the micrographs of the eletrogalvanized steel used: (a) without surface treatment; (b) passivated in solution with Cr^{6+}. The cracked morphology of the chromate layer is seen and the irregularities of the zinc substrate are identifiable on the coated surface due to the low thickness of the conversion layer. The surface of one sample sequentially treated in solutions with cerium and ANO and immersed for 1 day in 0.1 M NaCl is shown Fig. 1 (c) and the EDS spectrum corresponding to the area indicated by arrow, in Fig. 1(d).
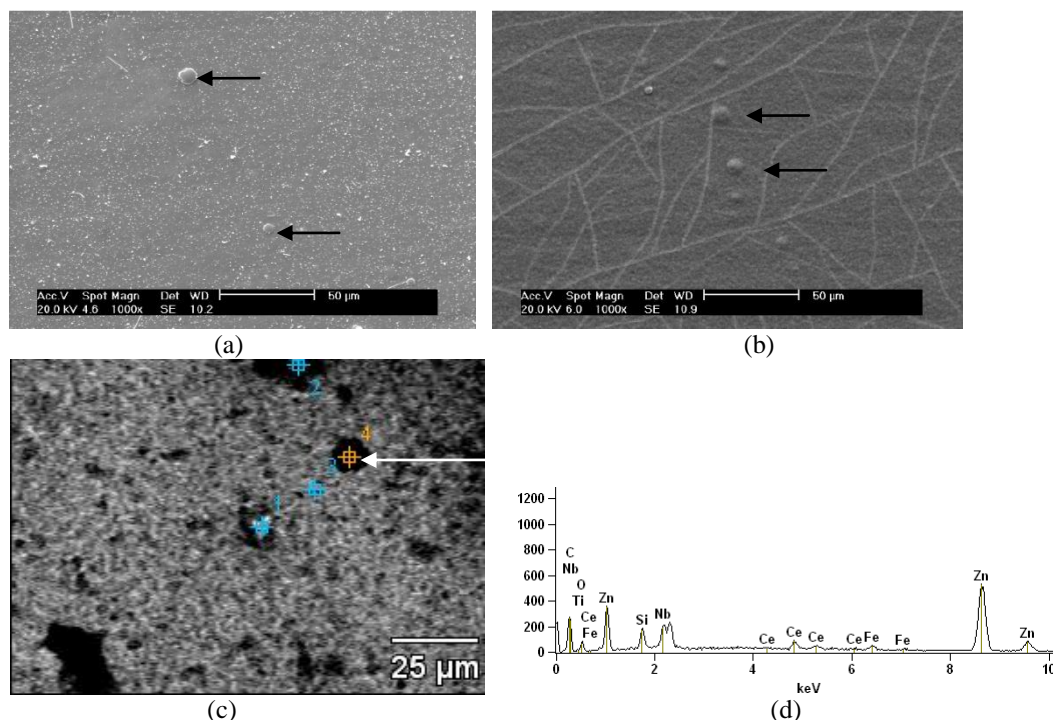
(a)   (b)

(c)   (d)

Fig. 1. SEM micrograph of eletrogalvanized steel surface: (a) without surface treatment; (b) with Cr^{6+} conversion coating; (c) treated in Ce solution and then in ammonium niobium oxalate and immersed for 1 day in 0.1 M NaCl solution; (d) EDS spectrum of the area marked as #4 in (c).

The EDS spectrum shows Zn from the substrate, Si from the electrodeposition process that contains silica for bath stabilization, and Nb and Ce from the surface treatment solutions. The proportionally high Nb concentration at the site analyzed was also found at other dark sites, suggesting that there is an increase in the Nb concentration at heterogeneities on the surface. Niobium was always detected at other surface areas even after 7 days of immersion showing that it remains for long periods of exposure to an aggressive medium. The results also show that a Ce containing layer is found on the surface after exposure to the corrosive conditions and might provide additional protection to the substrate, despite the surface film degradation with time indicated by EIS data, shown in Fig. 2. As this figure shows, for one day of immersion there is an indication of diffusion controlled processes at low frequencies, but this was not seen for longer periods of test.

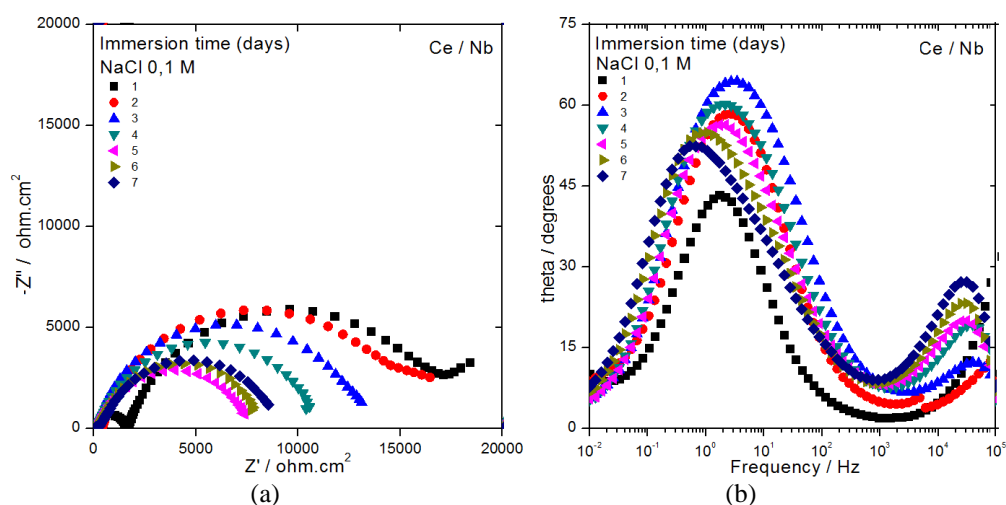(a)   (b)

Fig. 2: EIS results as a function of time of immersion in 0.1 M NaCl solution: (a) Nyquist diagrams; (b) Bode phase angle diagrams; for samples after surface treatments with Ce^{3+} and then Nb oxalate.

The EIS data also show that the impedance decreased with time between 1 and 5 days, and slightly increased from 5 to 7 days, suggesting that the passivating film degrades with time, exposing larger areas of the zinc substrate, and then, zinc corrosion products accumulate on the surface inhibiting the corrosion process. It is well known that some zinc corrosion products act as corrosion inhibitors explaining the slight increase in impedance between 5 and 7 days. The Bode phase angle diagrams clearly show two time constants, one at high frequencies (above 10^4 Hz), due to the outer Ce/Nb/Zn corrosion products protective layer, and another at medium frequencies (10 to 10^{-1} Hz), probably associated with charge transfer processes at the zinc substrate. The time constant at high frequencies increases and is displaced into lower frequencies with time of immersion and this is related to passive layer degradation with time of immersion in the electrolyte. The phase angle related to the time constant at medium frequencies was displaced to lower frequencies for periods longer than 3 days, indicating a slowing down of the charge transfer kinetics. This must be related to the accumulation of corrosion products increasingly hindering the access of corrosive species to the substrate.

EIS results for the surface treatments used and the zinc substrate without treatment are compared in Fig. 3 for 1 and 7 days of immersion. It is clearly seen that for this period of test, that the combination of Ce and ANO treatments led to much higher impedances comparatively to the Cr^{6+} conversion coating treatment. Although the first treatment was related to impedances at low frequencies about twice that of the Cr^{6+} type for 1 day of test, it was more than four times larger for 7 days, showing that with increasing exposure there is a greater difference in the performance of both treatments. The EIS results were supported by ASTM B117 salt spray tests. These also showed much improved corrosion resistance of the Ce^{3+} and ANO treated surfaces compared to the Cr^{6+} conversion coating. White corrosion products were firstly seen on the samples with Ce^{3+} and ANO treatment after 8 days, but were noticed on the chromated surface after 5 days. For the untreated surface, white corrosion products was noticed after only 2 hours of salt spray test.
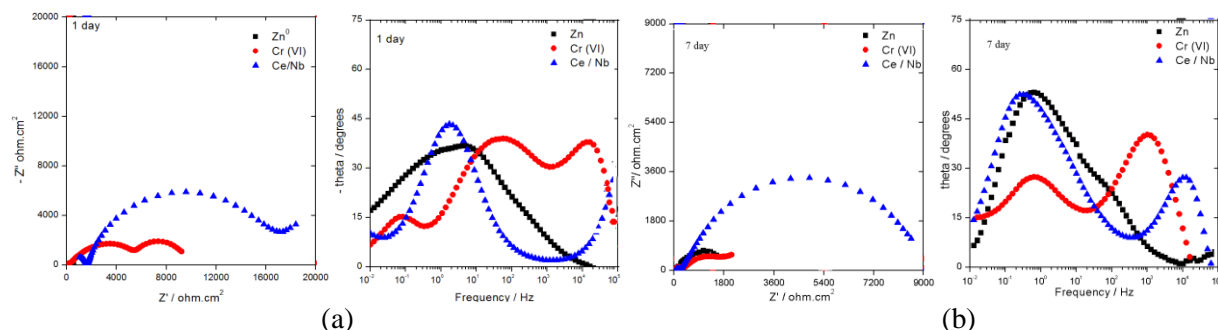

Fig. 3: EIS data for all surfaces tested after (a) 1 day and (b) 7 days of immersion in 0.1 M NaCl solution.

Conclusions

Salt spray results showed that a dual stage treatment of a Ce^{3+} aqueous solution followed by an ANO containing solution resulted in a surface with a higher corrosion resistance than that provided by a Cr^{6+} based conversion layer in 0.1 M NaCl solution. EIS results indicate that with increasing exposure time, the combined treatment offers improved protection compared to the Cr^{6+} based treatment.

Acknowledgements

References
1. Zumelzu, E., Rull, F., *Science and Engineering of Composite Materials*, **10** (2002) 345.
2. Fousse, D., Malle, P., Seurin, P., *Proc. of 7th Intern. Tinplate Conference, Amsterdam*, Holanda, 2000.
3. Treacy, G.M., Wilcox, G.D., Richardson, M.O.W., *J. of Appl. Electroch.*, **29** (1999) 647.
4. Veleva, L., Chin, J., Del Amo, B., *Progr. in Org. Coat.,* **36** (1999) 211.
5. Banckzek, E.P., Terada, M., Rodrigues, P.R.P., Costa, I., *Surf. & Coat. Techn.,* **205** (2010) 2503.