Passivation Treatments for Galvanized Steel as Potential Replacements to Chromate Conversion Coatings

<u>Marcelo Oliveira</u>, José Mário Ferreira Jr., Wagner I. A. dos Santos, Célia R. Tomachuk, Jesualdo L. Rossi, Isolda Costa Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, São Paulo, SP, 05508-000 - Brazil Email: m.marcelodeoliveira@yahoo.com.br

Introduction

Passivation with Cr^{VI} , such as those with dichromate or chromate ions [1,2] was for many years the most important conversion coating used in combination with zinc based coatings, producing chromium oxide or hydroxide on the substrate for its corrosion protection [1]. However, due to its inherent toxicity, the replacement of Cr^{VI} in surface treatments has been in the last decades a matter of investigation [3,4]. Passivation treatments in solutions with Cr^{III} have been used as alternatives to those with Cr^{VI} . However, Cr^{III} under certain conditions may oxidize to Cr^{VI} and the development of new chromium free passivation treatments is required [5,6]. In this study, the effect of ammonium niobium oxalate ANO (NH₄H₂[(NbO)(C₂O₄)₃]3H₂O), as a passivating agent and alternative surface treatment for corrosion protection and replacement of Cr^{VI} of electrogalvanized steel has been investigated.

Experimental

Samples of carbon steel SAE 1010 were used as substrates for zinc electrodeposition. After electrogalvanization and activation in HNO₃, these samples were immersed in a solution with ANO for passivation treatment. A surface passivation treatment with chromium ions was also adopted for comparison reasons using a solution with 200 mg L^{-1} Cr^{VI} ions at (35 ± 2) °C. The passivation with ANO was carried out in solutions with various concentrations of niobium, specifically 400 ppm, 800 ppm, and 1200 ppm. The pH of the passivation solutions with ANO was maintained at 4 by adding a buffer solution with NaH₂PO₄. Since the ANO has an acidic character, increasing amounts of buffer solution was added with the increasing concentration of ANO. Passivation was carried out by immersion in either of these solutions for 60 seconds. The morphology of the surfaces after passivation treatments was evaluated by scanning electron microscopy (SEM). The surface chemical composition was investigated by means of X-ray photoelectron spectroscopy (XPS). Electrochemical impedance spectroscopy (EIS) tests were carried out to evaluate the corrosion resistance of the samples after surface treatments. A threeelectrode set-up cell was used, with an Ag/AgCl and a platinum wire as reference and counter electrodes, respectively, was adopted for the electrochemical investigation. The electrolyte used was a 0.5 mol L⁻¹ NaCl solution at (23 ± 2) °C. All electrochemical impedance spectroscopy (EIS) measurements were performed in the potentiostatic mode at the corrosion potential. The amplitude of the perturbation signal was \pm 10 mV, and the frequency range investigated was from 100 kHz to 10 mHz with an acquisition rate of 10 points per decade.

Results

Fig. 1 shows SEM micrographs of the electrogalvanized steel activated in HNO_3 (Fig. 1a) and then passivated in chromate solution (Fig. 1b), respectively. The morphologies of the electrogalvanized steel passivated samples in ANO with 400 ppm, 800 ppm and 1200 ppm of niobium, are shown in Figs. 2 a, b, and c, respectively. The surface of the activated samples (Fig. 1a) shows irregularities such as particles that were covered by a cracked chromate film, resulting from passivation with Cr^{VI} ions. The treatments with ANO produced a smoother surface comparatively to that with Cr^{VI} . In fact, a more homogeneous and smoother surface was associated to the passivation in the solution with 800 ppm of ANO.



Figure 1: SEM micrographs of the electrogalvanized steel activated in HNO_3 (a) and then passivated in Cr^{VI} ions containing solution (b).



Figure 2: SEM micrographs the electrogalvanized steel passivated in solutions with ANO at concentrations of (a) 400 ppm, (b) 800 ppm and (c) 1200 ppm.

A comparison of the EIS data for all passivation treatments tested and the surface without passivation is shown in Figs. 3 and 4, as Nyquist and Bode phase angle diagrams, respectively at increasing immersion times (24, 48 and 72 hours).



Figure 3: Nyquist diagrams for electrogalvanized samples with or without passivation treatments in Cr^{VI} or ANO solutions in different concentration after 24 h (a), 48 h (b) and 72 h of the immersion (c).



Figure 4: Bode diagrams for samples with treatment in ANO solutions in different concentration after 24 h (a), 48 h (b) and 72 h of the immersion (c).

The Nyquist diagrams show that the highest impedances for 24 h of immersion were associated to the passivation with ANO solution with 400 ppm, followed by the treatment with 800 ppm.

However, for longer periods, the surface treated with ANO solution with 400 ppm showed a significant decrease of impedance whereas the treatment with ANO 800 ppm produce a much stable surface and after 72 h of test this surface was associated to the highest impedance among the samples tested. These results suggest that the phosphate ions in the buffer solution might compete for the surface with the components of the ANO solution leading to an optimum concentration related to an optimum ANO-surface interaction for corrosion protection.

The Bode phase angle diagrams for the passivated samples at 24 h of immersion present two time constants, one related to the passive film, and the second at lower frequencies, due to mass transport. At periods corresponding to 48 h and 72 h a third time constant at intermediate frequencies appears in the diagrams, not well defined in some cases, as for the passivated samples with ANO (800 ppm). The time constant at intermediate frequencies might be related to the corrosive process. The evolution of the results at this frequency range revealed that its corresponding capacitance increased with time in a similar way as it was observed with the bare zinc surface, that is, the time constant was seen at progressively lower frequencies and the corresponding capacitance increased with time. However, for the samples passivated with ANO (800 ppm), the results clearly show a very stable surface. The protective properties of this last type of passive film were preserved throughout the period of test.

It is important to mention that the effect of self-healing associated to the samples passivated with Cr^{VI} was indicated in the EIS results. The Bode phase angle diagrams showed that between 24 h and 48 h of test a third time constant at intermediate frequencies appears and the impedance slightly increased between 48 h and 72 h of immersion, as indicated in the inserts of Fig. 3. This is related to the self-healing process. Despite of this, the barrier properties of the passive film formed on the surface treated with ANO (800 ppm) was superior to that of the chromate layer during the whole test period suggesting that this could be further investigated as a potential replacement for chromate conversion coatings.

Surface analysis carried out by SEM and XPS (results not presented here) show the presence of nitrogen, carbon, niobium, phosphorus, zinc and oxygen. The quantity of nitrogen increased with the increased amount of buffer added into the solution. The carbon peaks showed characteristics of the non-aliphatic group, probably group acetate or oxalate. The niobium peaks show two chemical states, Nb⁺⁴ and Nb⁺⁵ at similar concentrations, but were found at low contents in the passive film. The concentrations of zinc suggested that substrate is more exposed in the sample prepared in the ANO solution with 1200 ppm of niobium, what explains the inferior performance of the samples treated in this solution comparatively to that with 400 ppm or 800 ppm. Further investigation is underway to characterize the surfaces treated in the various types of passivating solutions.

Conclusions

The results showed that the treatment by immersion in solution with 800 ppm of ammonium niobium oxalate (ANO) and at pH 4 resulted in a very stable passivating film that largely increased the impedance of electrogalvanized samples. Despite of lacking self-healing properties, its barrier properties were much superior to that of the chromate layer obtained by conversion treatment with Cr^{VI} ions. This treatment with ANO suggested potential properties for use as possible replacement for chromate conversion coating.

Acknowledgements

The authors are grateful to CNPq for the grant provided to one of the authors (J.M. Ferreira Jr.).

References

[1] D. Fousse, P. Malle, P. Seurin, Proceeding of 7th Intern. Tinplate Conference, Amsterdam, Holanda, 2000.

[2] G. M. Treacy, G. D. Wilcox, M. O. W. Richardson, J. of Applied Electrochemistry, 29 (1999) 647.

[3] M. W. Kendig, A. J. Davenport, H. S. Isaacs, Corros. Sci. 34 (1993) 41.

[4] P. Campestrini, G. Goeminne, H. Terryn, J. Vereecken, J. H. W. de Wit, J. Electrochem. Soc. 151 (2004) B59.
[5] E. Zumelzu, C. Cabezas, A. Vera, Scanning, 25 (2003) 34.

[6] C. R. Tomachuk, C. I. Elsner, A. R. Di Sarli, O. B. Ferraz, Mater. Chem. and Physics 119 (2010) 19.