

Introduction

There is a great desire to find alternatives to SrCrO_4 inhibiting pigments in corrosion resistant coatings due to chromate toxicity. Efforts have also been aimed at adding new functionality to coatings such as early detection of undercoat corrosion or remaining coating protectiveness. In this paper, the use of cerium (III)-exchanged bentonite particulate additives to organic coatings for corrosion inhibition and corrosion sensing is described. Treatment of Al alloys with aqueous solutions of rare earth salts, especially cerium salts, effectively inhibits corrosion (1), and the use of Ce-exchanged bentonites as corrosion-inhibiting pigments in coatings has already been demonstrated by others (3-5). This study shows that upon cerium release, sodium in the attacking electrolyte is taken up by the bentonite inducing a change in the crystal structure that can be detected by X-ray diffraction methods. This phenomenon enables the coating to be interrogated remotely to assess inhibitor exhaustion and remaining corrosion protection.

Experimental

Ion exchange. Commercially obtained bentonite samples were exchanged with cerium (III) cations from aqueous solutions of cerium chloride by soaking 50 g of bentonite in 1 L of 0.3 M CeCl_3 solution with stirring for 1 h and continued quiescent immersion overnight. The solution was then changed, stirred for 1 h and left for 3 days. The exchanged bentonites were then filtered and washed until chloride ions could no longer be detected in the washing liquor. Final washing was carried out with ethyl alcohol. The resulting powder was ground in mortar and pestle.

Coating synthesis and application. Bentonite pigmented coatings were made by mixing cerium (III) cation exchanged bentonite powder into an amide-cured bisphenol epoxy resin conforming to MIL-PRF-23377. Bentonite was added to the resin component of the coating in amount of 25 wt%, and was applied to 2024-T3 (Al-4.4Cu-1.5Mg-0.6Mn) sheet stock coupons using a drawdown bar. One coat was applied. Coatings produced in this way were uniform in color and visually masked the underlying substrate. Coatings were allowed to cure for 1 week at room temperature and humidity before any corrosion testing.

Summary of Results

Ion exchange. Figure 1 shows XRD patterns of the bentonite powder before and after ion exchange. Layer separation in smectites depends both on the interlayer cation and the amount of water associated with it. Separation is readily measured from the (001) basal reflections (2). The interlayer cations are much more accessible than other cations in the structure and are replaced when the clay is wetted with a suitable salt solution (2). In this case, sodium is replaced with cerium, and a (001) basal reflection shift from 8.5° to 6.5° is observed. Higher intensity in Ce-bentonite (001) basal reflection is observed as compared to Na-bentonite.

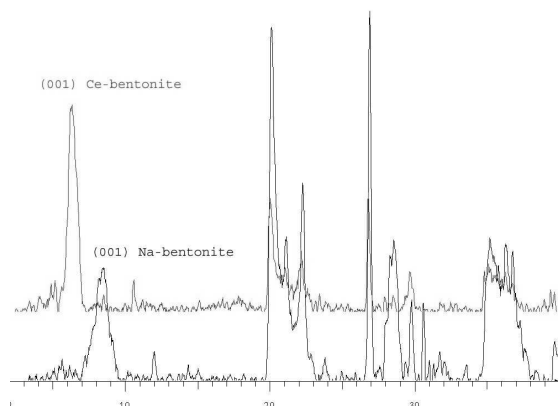


Figure 1. XRD pattern of the bentonite powder before and after ion exchange (x axis is 2θ).

Static exposure in 0.5 M NaCl. Figure 2 shows XRD pattern of the Ce-bentonite pigment coated on AA2024-T3 during exposure in 0.5 M NaCl up to 25 days. The pattern shows reflections from the bentonite pigment and from the Al substrate. Overlapping, but resolvable (001) reflections from the Na- and Ce-bentonite compounds are present at about $5^\circ 2\theta$. With increasing exposure time the reflection associated with the Ce-compound decreases in intensity while that for Na-bentonite increases. This indicates exchange of Ce cations and uptake of Na cations from the attacking electrolyte. In separate experiments, solution analysis confirmed Ce cation release. While the intensities of the two (001) peaks suggest Ce release, Ce exhaustion does not seem to have occurred during the course of this experiment.

EIS spectra show a two time constant response indicative of early-stage coating breakdown and substrate corrosion. However, from 5 to 20 days exposure, the pore resistance, coating capacitance, defect capacitance and total sample impedance do not change significantly and the overall sample impedance remains high (Figure 3). Such a response is consistent with a slightly degraded coating that is being protected by a released inhibitor.

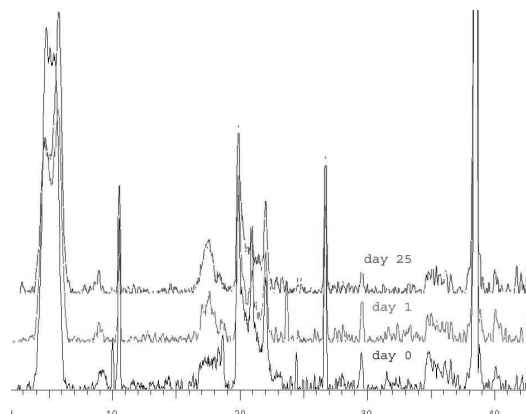


Figure 2. XRD pattern of the Ce-bentonite pigmented coating on AA2024-T3 during static exposure in 0.5 M NaCl up to 25 days (x axis is 2θ)

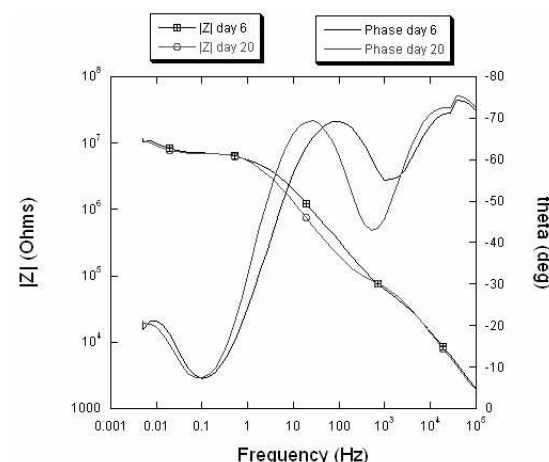


Figure 3. Bode plots of Ce-bentonite pigmented coating on AA2024-T3 during static immersion in 0.5 M NaCl up to 20 days.

These results show that Ce-exchanged bentonite pigments added to epoxy resins and applied as coatings to metallic substrates lead to corrosion protection while leading to a remote, XRD-based method for determining the extent of remaining inhibitor reservoir.

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References

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