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The Response of Hydrotalcite Coated Aluminum to Sealing with Transition Metal Salt Solutions

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Background

One approach to devising procedurally simple, environmentally acceptable schemes for depositing corrosion resistant coatings on aluminum alloys is to: 1.) form a thick aluminum oxide surface layer either chemically or electrolytically, then 2.) minimize residual porosity in the oxide layer using a pore filling sealing agent, or heal coating defects at intermetallic particles by formation of an insoluble oxide or hydroxide that precipitates in the local alkaline conditions at the solution-intermetallic interface. Sealed sulfuric acid anodized aluminum, and permanganate-sealed hydrothermal aluminum oxide are examples of how this methodology has been implemented successfully.

Inorganic polycrystalline hydrotalcite, $Li_2[Al_2(OH)_6]_2 \cdot CO_3 \cdot 3H_2O$, coatings can be formed rapidly on aluminum alloys by immersion in alkaline lithium salt solutions. These coatings are continuous across the aluminum surface and form in thicknesses of 0.1 to 10+ micrometers depending on alloy type and coating bath conditions. This coating process is essentially a chemical means for generating a complex hydrothermal oxide. The coatings contain intercrystalline spaces which are the structural analog to pores in anodized coatings. The objective of this study is to determine if the protective properties of this coating can be enhanced by filling intercrystalline spaces or by reinforcing the coating at intermetallic particles by exposing hydrotalcite coated aluminum alloys to aqueous transition metal salt solutions known to improve the protective properties of inorganic coatings on aluminum. Two widely studied oxy-anion analogs to chromate were selected for this study: permanganate (MnO_4^-), molybdate (MoO_4^{2-}) (1). Ce(III) (as $Ce(NO_3)_3$) was also selected because of its tendency to preferentially precipitate as an oxide or hydroxide at defect sites in oxide coatings (2).

Experimental Procedures

Aluminum alloys 2024-T3 (Al-4.4Cu-1.5Mg-0.6Mn) and 6061-T6 (Al-1.0Mg-0.6Si) were selected as substrate materials for this study. Panels 4" x 5" were prepared from commercially available 0.080" 6061 and 0.063" 2024 sheet stock. Mill finish panels were immersed in an alkaline lithium salt solution to form the hydrotalcite coating. The general methods for this process are described elsewhere (3). The panels were allowed to air dry for at least 24 hours prior to exposure to the transition metal salt baths. One tenth molar (0.1 M) salt solutions were prepared by adding the metal salt to a 0.1 M $LiNO_3$ base solution. The use of $LiNO_3$ was intended to minimize any hydrotalcite coating dissolution during the sealing step. Sealing baths were held at 50° C for the duration of the sealing process. Sealing times, metals salts and bath pH values are reported in Table 1. Identical procedures were used for 2024-T3 and 6061-T6 samples.

Sealed samples were allowed to air dry for at least 24 hours prior to testing. Coating barrier properties were determined using electrochemical impedance spectroscopy (EIS). Samples were exposed to aerated 0.5 M NaCl for 24±1 hours under free corrosion conditions using a standard flat cell arrangement that allowed 16 cm^2 of specimen area to be exposed. EIS experiments were conducted using a three electrode measurement at the free corrosion potential. A 10 mV sinusoidal voltage modulation was used over a frequency range of 10 kHz to 10 mHz.

Summary of Results

Figure 1 is a complex plane plot of hydrotalcite coated 6061-T6 sealed in each of the three metal salt solutions. In these tests corrosion resistance increases in the order:

$$Ce(III) < MoO_4^{2-} < MnO_4^-.$$

The total specimen resistance ranged from 150 to 350 kΩ-cm^2 which is not substantially greater than is achieved with unsealed talc coatings (3). A control experiment was conducted by exposing a 6061-T6 panel with no hydrotalcite coating to the MoO_4^{2-} sealing solution. The total impedance at 10 mHz was 6 kΩ-cm^2 indicating that the sealing alone could not be capable of substantially improving corrosion resistance. The EIS response indicated a single relaxation at intermediate frequencies due to the coating, and a transmission line response at low frequencies suggesting localized corrosion. Visual inspection after testing showed that localized attack occurred as crevice corrosion at the specimen-cell gasket interface.

Figure 2 is a complex plane plot of hydrotalcite coated 2024-T3 sealed in the three metal salt solutions. Here corrosion resistance increases in the order:

$$MnO_4^- < MoO_4^{2-} < Ce(III)$$

which is opposite for the trend observed for talc coated 6061-T6. In this case, sealing does result in an improvement in the protective properties compared to unsealed talc coatings. The relative contributions to protection are shown in Figures 3 and 4 which show Bode magnitude and Bode phase angle plots for hydrotalcite coated, Ce(III) sealed-only and hydrotalcite-coated and sealed 2024-T3 surfaces. Use of the sealing step alone improves corrosion resistance, but sealing combined with hydrotalcite coating offers a further factor of 3 improvement in corrosion resistance.

The Bode phase angle plot in Figure 4 shows that a second time constant is present at intermediate frequencies (~ 1 Hz), that is not observed in the sealed-only or talc coated-only samples. The two time constant behavior is consistent with the response expected from a hydrotalcite coated surface with coating defect sites that have been partially blocked by precipitation of cerium oxides or hydroxides.

Ce(III) sealed hydrotalcite coated 2024-T3 samples prepared as described above pit under salt spray exposure conditions, but suffer far less damage than unsealed samples. Efforts to further exploit the beneficial effects of Ce(III) sealing of hydrotalcite coated 2024-T3 are currently underway.

References

1.) B.R.W. Hinton, Metal Finishing, Sept. (1991), p. 55

2.) D.R. Arnott, B.W.R. Hinton, Corrosion, 45 (1989), p. 12.

3.) R.G. Buchheit, M.D. Bode, G.E. Stoner, Corrosion, 50 (1994), p. 205.

Acknowledgments

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Table 1. Details of the sealing baths for hydrotalcite coated samples.

Metal	Compound	Bath pH	Immersion Time (sec)
Cerium	$Ce(NO_3)_3$	4.5	800
Manganese	$NaMnO_4$	7.0	600
Molybdenum	Li_2MoO_4	6.5	800

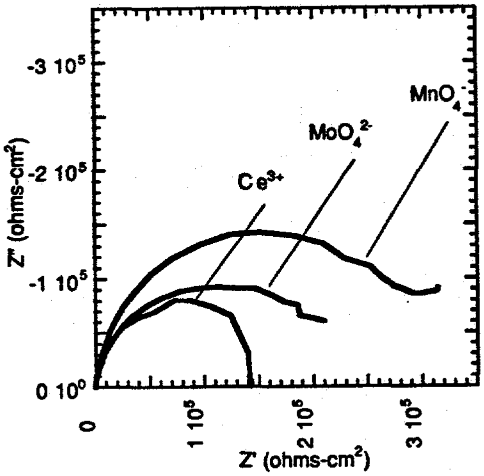

Figure 1. Complex plane plots for hydrotalcite coated 6061-T6 sealed in the three metal salt solutions.

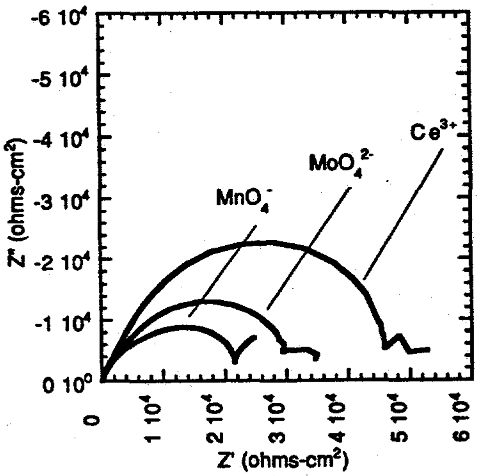

Figure 2. Complex plane plots for hydrotalcite coated 2024-T3 sealed in the three metal salt solutions.

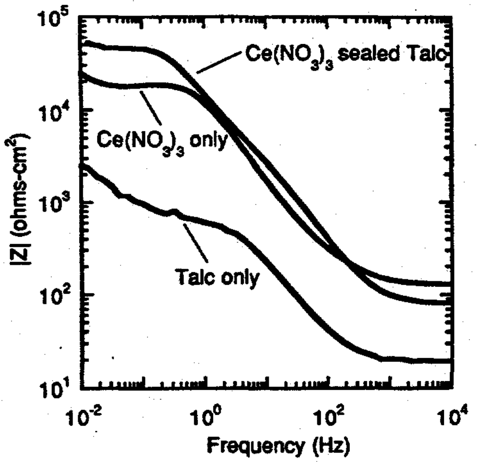

Figure 3. Bode magnitude plots for 2024-T3 with various treatments relevant to Ce(III) sealing.

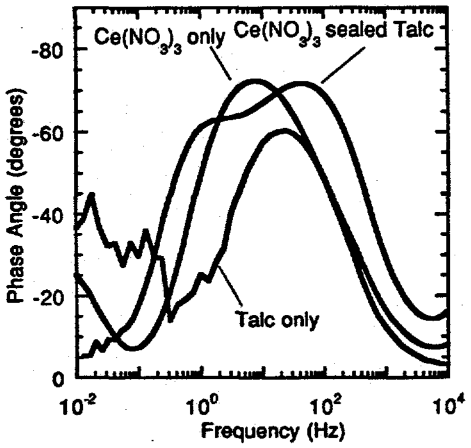

Figure 4. Bode phase angle plots for 2024-T3 with various treatments relevant to Ce(III) sealing.

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