CHROMATE-FREE CORROSION RESISTANT CONVERSION COATINGS FOR ALUMINUM ALLOYS

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Abstract

Inorganic polycrystalline hydrotalcite, Li$_2$[Al$_2$(OH)$_6$]$_2$CO$_3$·3H$_2$O, coatings can be formed on aluminum and aluminum alloys by exposure to alkaline lithium carbonate solutions. This process is conducted using methods similar to traditional chromate conversion coating procedures, but does not use or produce toxic chemicals. The coating provides anodic protection and delays the onset of pitting during anodic polarization. Cathodic reactions are also inhibited which may also contribute to corrosion protection. Recent studies have shown that corrosion resistance can be increased by sealing hydrotalcite coated surfaces to transition metal salt solutions including Ce(NO$_3$)$_3$, KMnO$_4$ and Na$_2$MoO$_4$. Results from these studies are also reported.

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Introduction

Thickening of aluminum oxides films by hydrothermal exposure is well known (1-3) and is exploited in methods for promoting corrosion resistance of aluminum alloys (1,4-6). Oxide film formation by hydrothermal exposure is common to many of the procedurally simple, environmentally friendly coating methods under development. When required, additional corrosion resistance is obtained by sealing hydrothermal coatings to fill pore spaces intrinsic to hydrothermal oxide layers, or to reinforce the coating imperfections that occur at intermetallic particles in the alloy surface.

Inorganic polycrystalline hydrotalcite (hereafter referred to as ‘talc’) Li$_2$[Al$_2$(OH)$_6$]$_2$CO$_3$·3H$_2$O, coatings can be formed rapidly by precipitation on aluminum alloy surfaces during immersion in alkaline lithium salt solutions at temperatures up to 100° C. Since the coating forms by precipitation under conditions where aluminum is normally quite soluble, the process is essentially a chemically stimulated method of forming a complex hydrothermal oxide. The coatings offer desirable properties including enhanced corrosion resistance, low electrical contact resistance and good paint adhesion (7). Additionally, lithium salts are low toxicity non-carcinogens and are not subject to strict environmental regulations.

In this paper, methods for depositing hydrothermal talc coatings are described. A summary of coating characteristics and properties is also provided. The mechanism of corrosion protection offered by the talc coating is addressed, and results from recent work aimed at enhancing corrosion resistance by sealing talc coatings using transition metal salt solutions are reported.

Experimental Procedures

Coating Methods

Talc Coatings. Talc coatings were formed on aluminum alloy coupons prepared from 1100 (Al-1.0(Fe,Cu,Si)), 2024-T3 (Al-4.4Cu-1.5Mg-0.6Mn), 5052 (Al-2.5Mg-0.25Cr), 6061-T6 (Al-1.0Mg-0.6Si), and 7075-T6 (Al-5.6Zn-2.5Mg-1.6Cu) sheet stock. Panels were prepared for coating by manually washing using a water-soluble alkaline detergent, degreasing with an alkaline non-etching solution and deoxidizing with an acid HNO$_3$/NaBr bath. Rinsing in flowing distilled water was performed in between each step. Coating was performed by immersion in an aqueous lithium salt solution with a pH of 11.2 to 11.5 at ambient temperatures or at a temperature controlled to 55±3° C. Because the coating forms by a co-precipitation reaction involving aluminate (Al(OH)$_4^-$), the bath was conditioned by adding 200 ppm aluminate as sodium aluminate (NaO-AlO) or potassium aluminate (KaO-AlO) upon make-up of new bath solution. Once prepared, coupons were immersed for a minimum of 5 minutes to form the coating, removed, rinsed and allowed to air dry. Coupons were allowed to age undisturbed for a minimum of 24 hours prior to any further handling.

For sealing experiments, 2024-T3 and 6061-T6 mill finish panels were immersed in an alkaline lithium salt solution to form the hydrotalcite coating as described above. 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±5° 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.

Electrochemical Corrosion Testing

Potentiodynamic Polarization. Anodic and cathodic polarization curves were determined for coated and uncoated samples in 0.5M NaCl solutions. Curves were acquired potentiodynamically using a PAR Model 173 Potentiostat/Galvanostat controlled by an electrochemical experiment software package installed on a personal computer (8).
Table I. Details of the sealing baths for hydrotalcite coated samples.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Compound</th>
<th>Bath pH</th>
<th>Immersion Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium</td>
<td>Ce(NO$_3$)$_3$</td>
<td>4.5</td>
<td>800</td>
</tr>
<tr>
<td>Manganese</td>
<td>NaMnO$_4$</td>
<td>7.0</td>
<td>600</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Li$_2$MoO$_4$</td>
<td>6.5</td>
<td>800</td>
</tr>
</tbody>
</table>

A standard three electrode configuration was used in a 300 cm$^3$ cylindrical Plexiglas flat cell with a 1.0 cm$^2$ port for exposing the test electrode surface. A scan rate of 0.2 mV/sec was used for acquiring all potentiodynamic scans. Potentials were referenced versus the saturated calomel electrode (sce). Scans for anodic polarization curves were initiated 0.04 to 0.1 V negative of the corrosion potential ($E_{corr}$) and continued to an arbitrary potential slightly positive of the breakaway potential ($E_{br}$). Scans for cathodic curves were initiated 0.05 V positive to $E_{corr}$ and continued to -2.5 V$_{sce}$.

Electrochemical Impedance Spectroscopy (EIS). The barrier properties of talc coatings were evaluated in 0.5 M NaCl solutions under free corrosion conditions using EIS. Measurements were carried out in a flat cell modified to accommodate a specimen with a 1.0, 16 or 20 cm$^2$ exposed area. Data were collected using either a PAR 273 potentiostat/Solartron 1255 frequency response analyzer (FRA) combination, or a Solartron 1286 electrochemical interface/1250 FRA combination. Each system was controlled by an impedance software package installed on a personal computer (9). Typically, measurements were made at frequencies ranging from 65 kHz to 0.5 mHz by sampling at 10 points per decade frequency using either a 10 or 20 mV sinusoidal voltage perturbation. Total resistances were determined either by circle fitting the data plotted in the complex plane, or by using a partial Kramers-Kronig transformation method (10). Total capacitances were determined from the slope of the $\chi''(\omega)$ vs. $\omega$ plot.

Results

Talc Coating Characterization

Grazing incident angle X-ray diffraction of talc coated surfaces show that the predominant compound in the coating is hydrotalcite. The carbonate anion in the hydrotalcite structure can be replaced by hydroxyl or chloride without a detectable change in diffraction patterns collected under standard conditions. As a result, the presence of isomorphic hydrotalcite variants can not be ruled out. Figure 1 is a plan view scanning electron micrograph that shows the typical morphology of the talc coating. The coating is comprised of intersecting crystallites that form a continuous layer across the aluminum alloy surface. Breaks are occasionally observed at large intermetallic inclusions particularly in Al-Cu-Mg-Mn alloys. Transmission electron microscopy of a coating cross section in Figure 2 shows that the intercrystalline spaces observed in Figure 1 do not penetrate to the coating-metal interface.

Coated surfaces typically exhibit a uniform matte finish, and the presence of a white translucent coating is apparent. Talc coating thicknesses range from 0.5 to 10$^+ \mu$m and have been observed to depend on alloy composition (11), coating bath composition and age (12), and immersion time (12). For 1100 Al and 6061-T6, typical coating thicknesses range from 1 to 3 $\mu$m for immersion times of 15 minutes. Coating thicknesses in excess of 10 $\mu$m have been observed for immersion times of 3 to 5 hours.

Corrosion Resistance of Hydrothermal Talc Coatings

Electrochemical Testing. Figure 3 shows anodic polarization curves for uncoated and talc coated 1100 Al in aerated 0.5 M NaCl solution. The curve for uncoated Al exhibits no passive region at potentials positive to $E_{corr}$ (at -0.700 V) indicating that the $E_{corr}$ is at or positive to $E_{br}$. $E_{corr}$ for talc coated Al is shifted in the negative direction and passive behavior is observed up
to a potential of about -0.580 V. This comparison shows that the talc coating promotes corrosion resistance in chloride solutions by inhibiting the anodic portion of the corrosion process.

Figure 1. Plan view scanning electron micrograph of talc coated 1100 Al.

Figure 2. Cross sectional view transmission electron micrograph of talc coated 1100 Al.

Figure 4 shows cathodic polarization curves for uncoated and talc coated 1100 Al in aerated 0.5 M NaCl solution. Overall, the kinetics of reduction reactions are slower than on uncoated Al as evidenced by lower cathodic current densities observed at all but the most negative applied potentials. Under free corrosion conditions, cathodic current supporting localized anodic dissolution must be provided by reduction reactions occurring elsewhere. Since reduction reactions are suppressed on talc-coated Al surfaces, the corrosion process may be cathodically limited under the proper conditions.

Figure 3. Anodic polarization curves for (1) uncoated Al, and (2) talc-coated Al in aerated 0.5 M NaCl solution.

Figure 4. Cathodic polarization curves for (1) uncoated Al and (2) talc-coated Al in aerated 0.5 M NaCl solution.
Figure 5 shows representative Bode plots for uncoated and talc coated 1100 Al after 72 hours exposure to aerated 0.5 M NaCl solution. The talc coated sample exhibits a capacitive response over a much broader frequency range than the uncoated sample due to the corrosion protection provided by the talc coating. The talc coated sample shown here exhibited a total resistance of $7 \times 10^5$ ohms-cm$^2$ as determined using the partial Kramers-Kronig method. This was more than two orders of magnitude greater than that for the uncoated sample.

Long term exposure of talc-coated 1100 Al to aerated 0.5 M NaCl solution shows that barrier properties of the coating are retained for approximately 80 hours. Figure 7 shows $E_{\text{corr}}$, total resistance ($R_t$), and total capacitance ($C_t$) as a function of exposure time up to 425 hours (17.7 days). After 80 hours exposure $E_{\text{corr}}$ falls from -0.750 $V_{\text{SCE}}$ to -0.975 $V_{\text{SCE}}$ while the $C_t$ increases from 5.5 $\mu$F/cm$^2$ to a peak of about 10 $\mu$F/cm$^2$. $R_t$ exhibits a sharp decline between 50 and 125 hours. The decrease in corrosion potential, increase in total capacitance and decrease in total resistance indicate failure of coating by pitting at about 80 hours. The slight increase in $R_t$ after 125 hours is attributed to the formation of a hydrated aluminum gel that was observed at the specimen surface. Examination of the exposed surface after testing confirmed that pitting had occurred during the test.
Figure 6. $E_{\text{corr}}$ (triangles), $R_t$ (circles), and $C_t$ (squares) versus time for talc-coated 1100 Al in aerated 0.5 M NaCl solution.

Table II. Summary of salt spray test results.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cu</th>
<th>Mg</th>
<th>Zn</th>
<th>Si</th>
<th>Coating Time (minutes)</th>
<th>Salt Spray Result</th>
<th>Maximum Time Tested (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5052</td>
<td></td>
<td>2.5</td>
<td></td>
<td></td>
<td>&lt;5</td>
<td>pass</td>
<td>168</td>
</tr>
<tr>
<td>1100</td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>pass</td>
<td>336</td>
</tr>
<tr>
<td>6061-T6</td>
<td></td>
<td>1.0</td>
<td></td>
<td>0.6</td>
<td>10</td>
<td>pass</td>
<td>336</td>
</tr>
<tr>
<td>7075-T6</td>
<td>1.6</td>
<td>2.5</td>
<td>5.6</td>
<td>1.6</td>
<td>300</td>
<td>pass</td>
<td>168</td>
</tr>
<tr>
<td>2024-T3</td>
<td>4.4</td>
<td>1.5</td>
<td></td>
<td></td>
<td>900</td>
<td>fail</td>
<td>168</td>
</tr>
</tbody>
</table>

Corrosion Resistance of Sealed Hydrothermal Talc Coatings

Recently, studies have been conducted to determine if the protective properties of talc coatings 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 other inorganic coatings on aluminum. Two widely studied oxy-anion analogs to chromate were selected for this study: permanganate ($\text{MnO}_4^-$) and molybdate ($\text{MoO}_4^{2-}$) (15). 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 (16).

Figure 7 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:

$$\text{Ce(III)} < \text{MoO}_4^{2-} < \text{MnO}_4^-.$$
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 8 is a complex plane plot of hydrotalcite coated 2024-T3 sealed in the three metal salt solutions. Here corrosion resistance increases in the order:

\[
\text{MnO}_4^- < \text{MoO}_4^{2-} < \text{Ce(III)}
\]

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 9 and 10 which show Bode magnitude and Bode phase angle plots for the hydrotalcite coated, Ce(III) sealed-only, and hydrotalcite-coated and Ce(III) 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 10 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.

![Figure 7. Complex plane plots for hydrotalcite coated 6061-T6 sealed in the three metal salt solutions.](image-url)
Figure 8. Complex plane plots for hydrotalcite coated 2024-T3 sealed in the three metal salt solutions.

Figure 9. Bode magnitude plots for 2024-T3 with various treatments relevant to Ce(III) sealing. Differences in Log|Z| are due to specimen area normalization.
Polycrystalline hydrothermal oxide coatings may be deposited on aluminum and aluminum alloys from an alkaline lithium salt solution. This coating method is procedurally similar to traditional coating processes but does not use toxic or hazardous chemicals. The coating promotes corrosion resistance by inhibiting both anodic and cathodic reactions involved in the localized corrosion process. Corrosion protection of talc coatings is sufficient to inhibit pitting on 1100 Al and 6061-T6 (Al-Si-Mg) during salt spray exposure testing. Electrochemical testing shows that sealing hydrothermal talc coatings can enhance corrosion resistance, particularly on aluminum alloys with high copper contents.

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References


