

Chromate-Free Corrosion Resistant Talc Coatings for Aluminum Alloys

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Background. The use of chromate conversion processes is expected to be increasingly restricted in the near future. Chromate conversion requires the use of hexavalent chromium which is a known carcinogen¹. Other toxic chemicals including cyanide and fluoride can also be present in commercial chromate conversion bath formulations. Because of increasingly stringent environmental regulations, replacement of chromate conversion processes is a high priority. However, implementation of a replacement process or processes depends on the development of suitable substitute technologies.

Aluminum exhibits unexpected passivity in alkaline solutions containing dissolved lithium salts^{2,3,4}. This phenomenon has been attributed to the formation of a surface film. We have shown that passivity developed by immersion in an alkaline lithium salt solution is retained when the aluminum surface is exposed to an aggressive solution like aerated NaCl. On this basis, we have developed a process for coating aluminum using a method that is procedurally similar to the chromate conversion process, imparts appreciable corrosion resistance, but does not use or produce hazardous chemicals.

Coating Formation and Characterization. Coatings have been formed on a variety of commercial Al-alloys. Specimens are prepared for coating in the usual manner by alkaline cleaning and acid deoxidizing. Coatings are formed by immersion in 0.1 M Li_2CO_3 solution whose pH is adjusted to 11.5 - 12.0 by additions of LiOH. To date, we have used immersion times ranging from 1.5 to 90 minutes to produce talc coatings. In our current best practice we use an immersion time of 15 minutes. Increased corrosion resistance is observed if the coating is sealed by an elevated temperature treatment in air or distilled water. The sealing treatment, at temperatures as low as 60° C for times as short as 15 minutes, produces improvements in corrosion resistance.

X-ray diffraction patterns generated from coated Al surfaces show that the film formed is polycrystalline and exhibits the structure of a talc compound whose stoichiometry is consistent with $\text{Li}_2[\text{Al}_2(\text{OH})_6]_2 \cdot \text{CO}_3 \cdot 3\text{H}_2\text{O}$. Scanning electron microscopy shows that the film is continuous and is comprised of a network of intersecting blade-like crystallites. Sputter depth profiles of films

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formed in the manner described above show that coating thicknesses range from 0.8 to 1.8 μm .

Talc formation occurs by a precipitation reaction involving aluminum, lithium, carbonate, hydroxyl ions⁵. Talc formation has been detected in solutions whose pH is as low as 8. However, only in strongly alkaline solutions, pH 10.0 and greater, are the concentrations of aluminum and carbonate high enough for appreciable talc formation to occur.

Lithium appears to be unique in its ability to participate in formation of talc films on aluminum. Group 1A metal salts are highly soluble in alkaline solutions, but do not readily form talc compounds. Group 2A metals are strong talc formers, but are insoluble in alkaline solutions where they precipitate as carbonates. Lithium, as the first member in its Group, has a small ionic radius and poorly screened nuclear charge and exhibits chemical properties

of both Group 1A and 2A metals. As a result, only lithium has the requisite properties of solubility (0.17 M/l)⁶, and capacity to participate in talc film formation.

Barrier Properties. Corrosion resistance has been assessed using standard salt spray exposure testing, and electrochemical impedance spectroscopy (EIS). Talc coated Al (99.5%) and 6061-T6 (Al-Mg-Si) withstand 336 hours salt spray exposure. Talc coatings on 2024-T3, and 7075-T6 improve corrosion resistance compared to uncoated controls, but do not pass 168 hours of salt spray exposure.

EIS performed on talc coatings during exposure to aerated 0.5 M NaCl shows that corrosion resistance is significantly improved compared to uncoated Al, although failure by pitting eventually occurs. Total resistance exhibited by the talc coating is comparable to the total resistance exhibited by a commercial chromate conversion coating after 3 hours exposure to aerated 0.5 M NaCl (Figure 1). Sputter depth profiles obtained after 125 hours exposure to aerated 0.5 M NaCl indicate that the outer coating is depleted of Al, Li, and C (from carbonate).

Beneficial effects of elevated temperature sealing are demonstrated in both EIS and SIMS data. EIS performed in a non-aggressive, supported electrolyte ($\text{Na}_2\text{B}_4\text{O}_7$ plus H_3BO_3 , pH 7) indicates that the film is intrinsically porous. EIS data suggest that the elevated temperature sealing treatment reduces porosity and increases corrosion resistance in chloride environments. SIMS data show that depletion of Al, Li, and C from the coating are strongly reduced by elevated temperature sealing.

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References

- 1.) Material Safety Data Sheet, Sodium Chromate (Na_2CrO_4).
- 2.) J. Gui, T.M. Devine, *Scripta Metall.*, 21, 853, 1987.

- 3.) J.G. Craig, R.C. Newman, M.R. Jarrett, N.J.H. Holroyd, J. Phys., 48, 825, 1987.
- 4.) C.M. Rangel, M.A. Travassos, Corrosion Sci., 33, 327, 1992.
- 5.) E.T. Iyagba, "A Study of the Crystal Structure of Hydrotalcites and Their Catalytic Properties", (Ph. D. Dissertation, University of Pittsburgh, 1986).
- 6.) R.C. Weast, ed., CRC Handbook of Chemistry and Physics, 67th Ed., CRC Press, Boca Raton, FL, 1986.

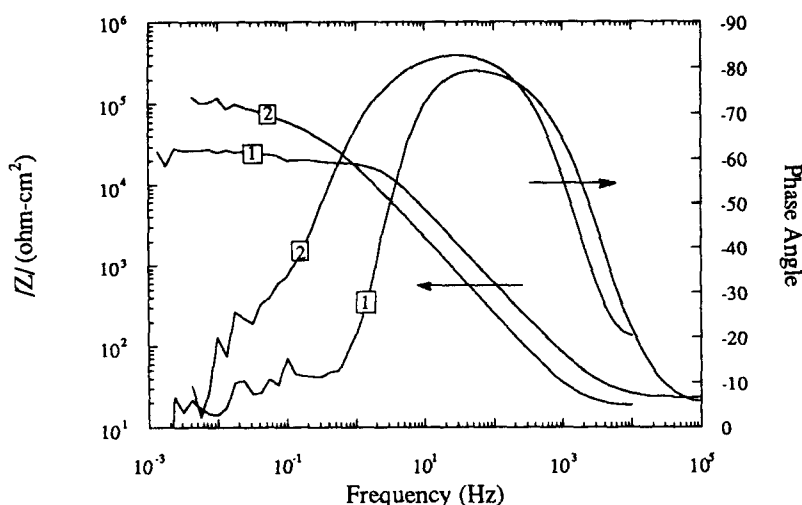


Figure 1. Impedance magnitude and phase angle for a commercial chromate conversion coating (1.) and for the talc coating (2.) on Al(99.5%) after 3 hours exposure to aerated 0.5 M NaCl solution

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