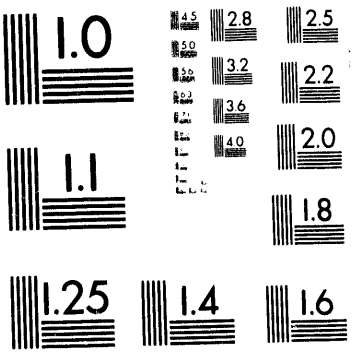
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ISSUES FOR CONVERSION COATING OF ALUMINUM ALLOYS WITH HYDROTALCITE*

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ABSTRACT

Hydrotalcite coatings on aluminum alloys are being developed for corrosion protection of aluminum in aggressive saline environments. The coating bath composition, surface pretreatment, and alloying elements in aluminum all influence the performance of these coatings during salt spray testing. The coating bath, comprised of lithium carbonate, requires aging by dissolution of aluminum into the bath in order to grow corrosion resistant coatings. Coatings formed in non-aged baths do not perform well in salt spray testing. The alloying elements in aluminum alloys, especially copper, influence the coating growth and formation leading to thin coatings. The effect of the alloy elements is to limit the supply of aluminum to the coating/electrolyte interface and hinder growth of hydrotalcite upon aluminum alloys.

Keywords: conversion coatings, aluminum alloys, surface analysis, acid de-oxidation, hydrotalcite

INTRODUCTION

Chromate conversion coatings for corrosion protection of aluminum alloys in aggressive saline environments have been used by industry for 40 years. However, the use of chromate conversion coatings is becoming limited by environmental issues dealing with the release of chromium into the environment, the carcinogenic nature of hexavalent chromium, and the banned use of cyanides in certain states. Replacements for chromate conversion coatings on aluminum alloys are being sought.

* This work was performed at Sandia National Laboratories, which is operated for the U. S. Department of Energy under contract number DE-AC04-~~76DP00789~~.
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One attractive alternative is the aluminum-lithium-carbonate-hydroxide-hydrate coating,[1] which may be formed using less environmentally hazardous materials. This alternative coating, referred to herein as hydrotalcite, is formed by immersion of aluminum into a lithium salt solution, generally lithium carbonate. The composition of the aluminum-lithium-carbonate-hydroxide-hydrate coating is thought to be $Al_4Li_2CO_3(OH)_{12}*3H_2O$. This new coating offers corrosion protection to Al 1100 and Al 6061-T6; and these alloys coated with hydrotalcite pass the ASTM B-117 salt spray test. The corrosion resistance is believed to be derived from the formation of a surface film with barrier properties.

Research and development of hydrotalcite coatings for aluminum alloys is ongoing in our laboratory. Factors affecting coating growth and formation are being determined, and the resulting corrosion behavior is being investigated. In this paper, the influences of surface pretreatment, coating bath composition, and alloy composition upon the hydrotalcite coating formation and coating performance are presented.

EXPERIMENTAL PROCEDURE

Hydrotalcite coatings were formed on aluminum alloy sheet stock--Al 1100, Al 2024-T3, Al 6061-T6, and Al 7075-T6--by immersing 4"x5"x0.125" (10.15 cm x 12.7 cm x 0.317 cm) coupons into a room temperature bath of 0.1 M Li_2CO_3 or 0.1 M Li_2CO_3 and 0.3 M LiOH. Prior to coating, the coupons were subjected to the following surface pretreatment--immersion in acetone for removal of organic debris, immersion in an alkaline cleaning bath (65 °C) of 0.1 M Na_2CO_3 and 0.1 M $NaSiO_3$ for removal of inorganic debris, and immersion in concentrated nitric acid containing ammonium bifluoride for removal of the native oxide and any aluminum silicate that may have formed in the alkaline cleaning solution. Between each step, the coupons were rinsed in de-ionized water. The lithium and aluminum concentration of the coating baths were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and the carbonate content was measured by titration.

Coatings were examined for microstructure and composition. The surface microstructure was observed with a JEOL 6400 SEM operated at 15 kV, while the cross-sectional microstructure was observed in a JEOL 2000 FX TEM, operated at 200 kV and equipped with an EDS detector. Surfaces of the aluminum substrates were examined for Cu, Zn, and Mg enrichment using Auger electron spectroscopy; a Physical Electronics AES model 595 system was operated at 5 kV. Samples were sputtered at rates of 100 or 250 Å/min as calibrated against a silica standard. Argon ion laser Raman spectroscopy was performed at an excitation wavelength of 514 nm using a triple spectrograph with a charge coupled detector and a microscope attachment.

Salt spray tests, performed as per ASTM B-117,[2] were used to screen coating corrosion performance because this test must be passed if coatings are to be accepted by industry. Open circuit measurements were taken with a PAR Potentiostat/Galvanostat model 273 using PAR Corrware software.

RESULTS

Coating Parameters--Immersion of aluminum coupons into the coating bath led to vigorous hydrogen evolution from the coupon surface. It was observed that coatings of consistent thickness and appearance were obtained only after the coating bath was aged; therefore, the time until hydrogen evolution ceased was monitored for each subsequent sample. Samples were removed from coating bath when hydrogen evolution ceased and a new sample was introduced. The time until hydrogen evolution ceased is plotted per sample in Figure 1a, along with the aluminum concentration measured when the sample wasremoved from the bath. Time of hydrogen evolution per sample remained constant after approximately 7 samples, but the overall time involved to age the baths increased with increased pH. Aging of the bath was more rapid for a coating bath containing only lithium carbonate (pH=11) as compared to the bath whose pH was adjusted with lithium hydroxide to 12.6. Figure 1a shows that the coating bath containing lithium hydroxide additions required >3 times longer to age than the lithium carbonate bath.

Aging of the bath did not entail a change in pH or carbonate content; pH values for the fresh bath and the aged bath differed by less than 0.03, and the carbonate content of the bath remained at the level of saturation of carbon dioxide in the solution. Aging of the bath was necessary to raise the aluminum concentration of the bath to a value close to the solubility limit for bayerite ($Al(OH)_3$) in alkaline solutions (see Table 1 and Figure 1b); evidently, this assured formation and growth of the hydrotalcite by precipitation or nucleation and growth on the substrate surface. At pH of 11, the amount of dissolved aluminum ions in equilibrium with bayerite is 27 mg/L ($\log(Al^{3+}) = -3$), while the concentration measured as the time for hydrogen evolution became constant between consecutive samples was 80 mg/L ($\log (Al^{3+}) = -2.53$). The logarithm of the concentration of aluminum dissolved in a basic solution of pH 12 is -1.8 as shown in Figure 1 b. The value obtained from the aged coating solution (pH=12) was -1.2, suggesting that bayerite formation may precede or support the formation of the hydrotalcite coating.

Continued use of the bath or letting the bath sit led to precipitation of hydrotalcite in solution. The concentration of aluminum left in solution after complete precipitation of hydrotalcite from an aged 0.1 M Li_2CO_3 bath was $8x10^{-6}$ M ($\log [Al^{3+}]=-5.09$), which is less than the value necessary to precipitate bayerite or gibbsite in alkaline solutions of pH =11. Analysis of the precipitate yielded 100% hydrotalcite whose aluminum to lithium composition ratio was 1.9 to 1, nearly that of $Al_4Li_2CO_3(OH)_{12}*3H_2O$. It thus appears that the equilibrium favored the formation of hydrotalcite over the formation of aluminum hydroxides. This is advantageous to the coating of aluminum alloys with hydrotalcite.

The surface morphology of coatings formed in the lithium carbonate bath differed from those formed in the lithium carbonate/lithium hydroxide bath during the early stages of the aging process (see Figure 2 a&d), but appeared the same after the baths were aged (see Figure 2 c&f). Coatings from the lithium carbonate/lithium hydroxide bath failed salt spray testing, except for coatings formed after the bath was fully aged. Aged and unaged coatings from the 0.1 M lithium carbonate bath passed salt spray testing (see Table 1). Laser Raman spectroscopy showed bands from an aluminate species from the coatings formed in unaged baths, and hydrotalcite crystals on the aluminate species from coatings formed in aged baths. Figures 2 a&d, which are the first coatings formed in each bath, show the aluminate species, while Figures 2 b,c &e,f, which are the second and last coatings formed in each bath, show hydrotalcite on the aluminate. Thus, the salt spray test results may reflect the differences in composition or thicknesses between samples from unaged baths and aged baths. The influence of an aged bath upon the corrosion behavior of the coatings is not yet understood; but, the significance of the results is that acceptable coatings can be formed in shorter times by using a lithium carbonate bath with pH =11.

Surface Pretreatment--One consequence of copper and magnesium in aluminum alloys is their potential for enrichment in the native surface oxide encountered on aluminum. Magnesium enrichment is known to result from heat treatment at temperatures above 300 °C,[4] and copper enrichment has been reported after certain de-oxidizing treatments.[5,6] In Figure 3, sputter depth profiles through the oxide films on Al 2024-T3 after a.) degreasing and b.) de-oxidizing treatments showed enrichment of copper resulted from the de-oxidizing step. The enrichment could result from two possibilities:

(i.) copper contained in an aluminum alloy dissolves into solution along with the aluminum during residence in the de-oxidizing bath. Deposition of the more noble copper from solution onto the Al substrate leaves the surface enriched.[7]

or, (ii.) aluminum is selectively dissolved from the alloy in the de-oxidizing bath leaving copper enriched at the metal surface.[6]

Both mechanisms may be operative, however enrichment of copper on Al 1100 is possible if the aluminum is de-oxidized in a bath containing copper nitrate.[8]

The direct consequence of copper enrichment on the alloy surface was investigated by de-oxidizing Al 1100 in a copper containing de-oxidation bath, such that copper was enriched upon the surface. Samples with and without Cu surface enrichment were coated with hydrotalcite and subjected to salt spray testing. Samples with Cu enrichment suffered from discoloration and small pits, while samples without the enrichment showed no such effects.

Alloying Elements--The copper-containing aluminum alloy Al 2024-T3 coated with hydrotalcite failed salt spray testing. Sputter depth profile of hydrotalcite-coated Al 2024-T3 showed the presence of both Mg and Cu in the coating (Figure 3c), and AEM analysis yielded copper throughout the thickness of the Al 1100 samples (Figure 4c) that were de-oxidized in a bath containing copper nitrate and subsequently coated. The effect of copper upon the corrosion behavior may result from its influence upon coating formation and growth. The cross-sectional TEM micrographs in Figure 4 show a.) a thick coating that formed upon Al 1100 and b.) a thin coating on Al 2024-T3. The inner and outer layers that are so obvious in the Al 1100 microstructure are not readily apparent in the Al 2024-T3 microstructure. The inner layer comprises most of the coating, and only a few small crystals of the outer layer are visible (see arrow in Figure 4b). The thickness and microstructure of the coating deposited on the Al 1100 de-oxidized in Cu-containing de-oxidizing bath was similar to the Al 2024 coating; only a single layer was observed and the coating thickness was about 0.5 μm.

When coating Al 2024-T3 and Al 7075-T6, hydrogen evolution ceased within 4 minutes; therefore, the influence of potential on coating was investigated. The open circuit potential of each alloy in a 0.1 M lithium carbonate/0.3 M lithium hydroxide bath was monitored versus a saturated calomel electrode for 10,000 s. Figure 5 shows that the open circuit potential initially rose for all alloys and then stabilized at different potentials based upon alloy composition. The Al 1100 shows this behavior also, but the rise in potential is much more gradual than for the alloyed compositions and the rise is not as great in magnitude. The potentials to which the Al 2024-T3 and Al 7075-T6 rose were approaching the potential at which the hydrogen evolution reaction can no longer be supported in an alkaline solution of pH=12. The observed cessation of hydrogen evolution from Al 2024-T3 and Al 7075-T6 corresponded to this rise in potential. In fact, coating Al 1100 in 0.1 M Li_2CO_3/0.3 M LiOH under an applied potential of -0.697 V vs SCE did not lead to the formation of an outer layer in the coating and was therefore unsuccessful. However, coating of Al 2024-T3 in the coating bath under an applied potential of -1.6 V vs SCE was also unsuccessful. Therefore, it may be concluded that the influence of potential upon coating formation is a secondary effect.

The supply of aluminum seems to be the dominating factor for the coating formation and growth, and the need for hydrogen evolution is that it supports aluminum dissolution. If the solubility of bayerite or hydrotalcite in solution is locally exceeded, precipitation and/or nucleation and growth of hydrotalcite on the substrate occurs. For coating of aluminum alloys, two scenarios may be considered:

i.) the formation of the inner layer and a few crystals of the outer layer is achieved before the supply of aluminum is hindered by diffusion through the inner layer,

or, ii.) the formation of the inner layer shifts the potential to a level where the aluminum dissolution and hydrogen evolution are slowed, so that the coating growth rate is reduced.

More work needs to be directed towards establishing the mechanism of coating formation and the role of the alloy elements in the coating formation and corrosion processes.

CONCLUSIONS

Hydrotalcite coatings for aluminum are being developed through an understanding of the effects of i.) coating bath composition, ii.) surface enrichment of copper due to de-oxidation of copper-containing aluminum alloys, and iii.) alloy effects upon coating formation and growth and salt spray test results. Initial results showed that the coating bath composition affected the corrosion protection afforded by the coating and that aging of the coating bath was necessary to produce effective coatings.

Surface pretreatment led to copper enrichment in copper-containing aluminum alloys, and copper on the alloy surface was incorporated into the coating. Alloy elements affect the coating growth and formation, yielding thin coatings with no apparent corrosion protection on Al 2024-T3. The influence of the alloying elements may be to limit the supply of aluminum to the coating by hindering diffusion of aluminum through the inner layer of the coating and/or by forming an barrier layer that raises the open circuit potential to a level where the hydrogen evolution reaction and consequently aluminum dissolution is slow or can no longer be supported.

ACKNOWLEDGMENTS

The authors thank K. R. Zavadil, T. E. Neil, R. W. Buttry, G. Nelson, B. Chambers, P. Puissant, J. Barrera, D. Strall, J. Reich, C. Hills, T. Tribble, and G. Zender for their technical support.

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TABLE 1
SALT SPRAY TEST RESULTS AND ALUMINUM CONCENTRATION FROM AGING EXPERIMENTS

Sample No.	0.1 M Li_2CO_3 bath		0.1 M Li_2CO_3/0.3 M LiOH bath	
	Salt Spray Test	Al Content (mg/L)	Salt Spray Test	Al Content (mg/L)
1	P	14.2	F	131
2	P	31.5	F	680
3	P	40.1	F	990
4	P	48.5	F	1140
5	P	56.9	F	1350
6	P	68.9	F	1550
7	P	69.5	F	1700
8	P	80.5	F	1650
9	P	84.1	P	1780

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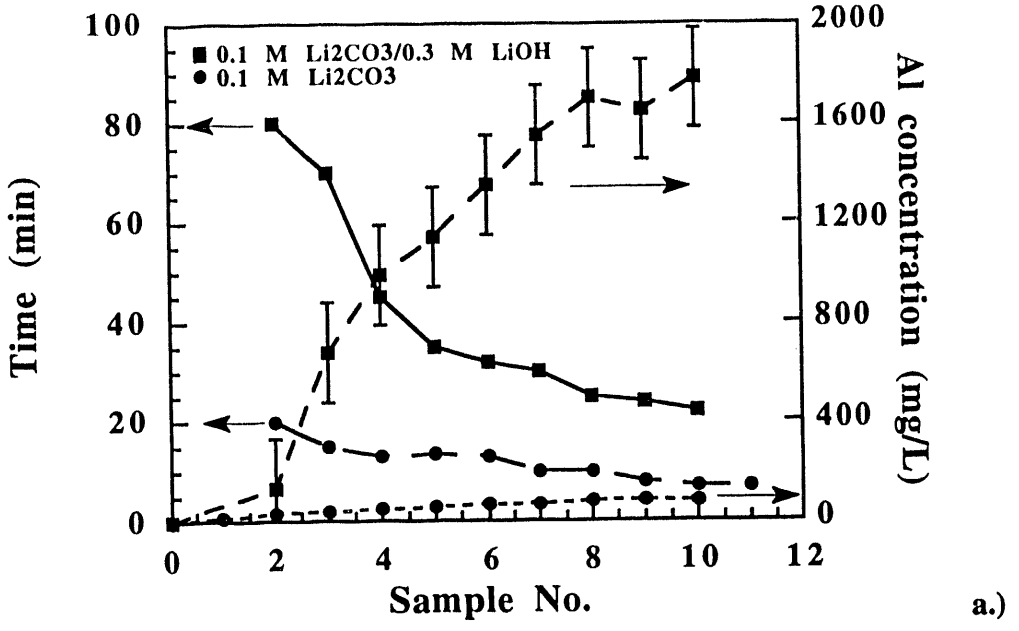
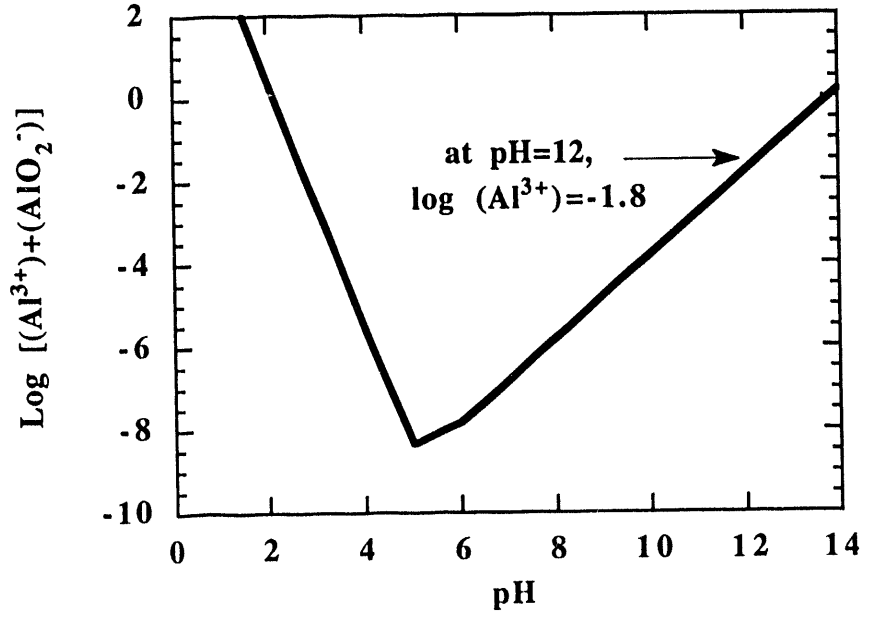


a.)



b.)

Figure 1.--a.) Time for hydrogen evolution to cease during coating Al 1100 in baths and aluminum concentration in 0.1 M Li_2CO_3/0.3 M LiOH bath versus sample number. b.) Aluminum ion concentration in solution vs pH due to dissolution of bayerite[9].

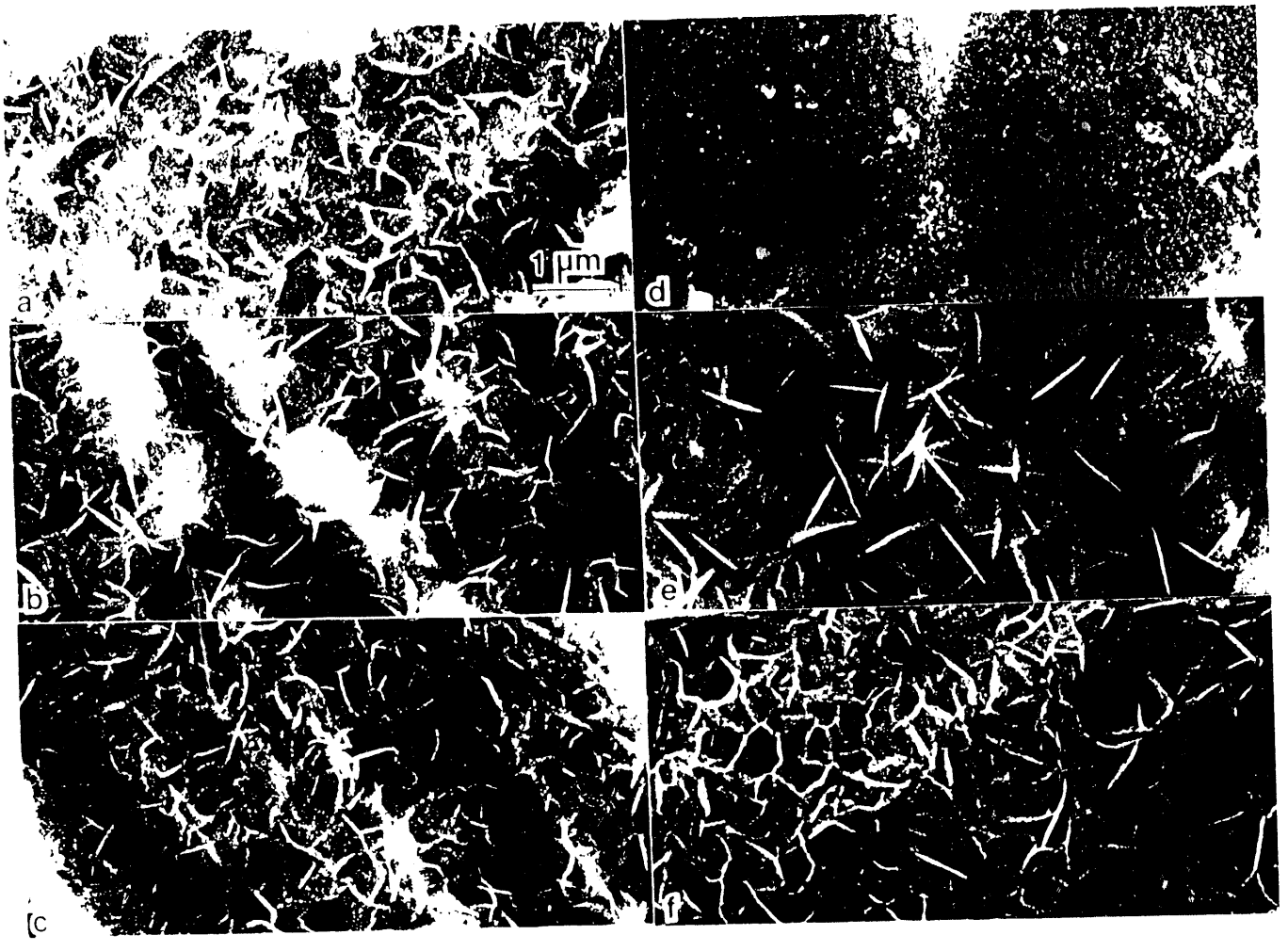
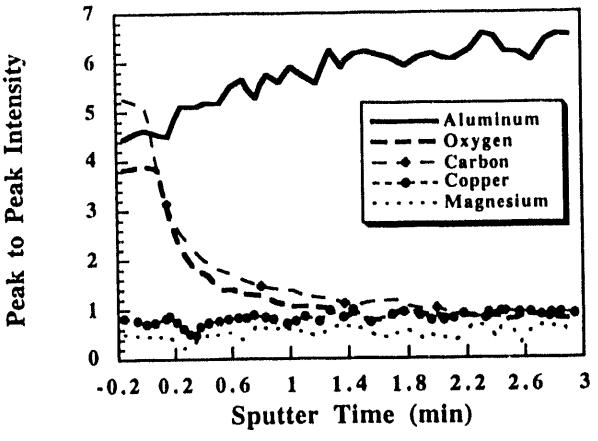
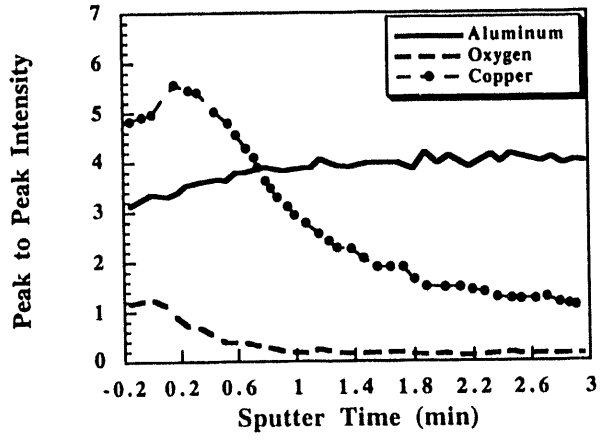


Figure 2.--Surface morphology of 1st, 2nd, and last 1100 Al samples coated in a-c.) 0.1 M Li_2CO_3 and d-f.) 0.1 M Li_2CO_3 and 0.3 M LiOH, respectively.





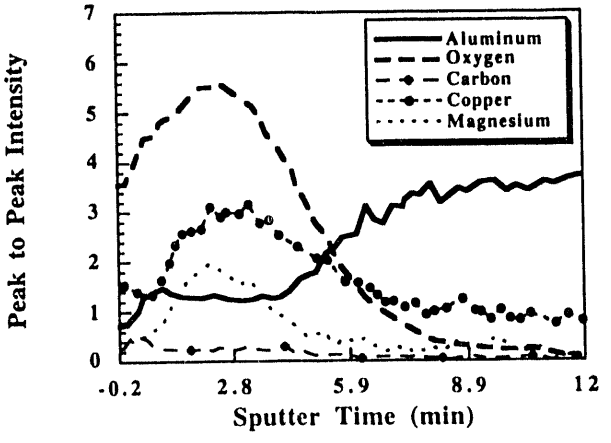
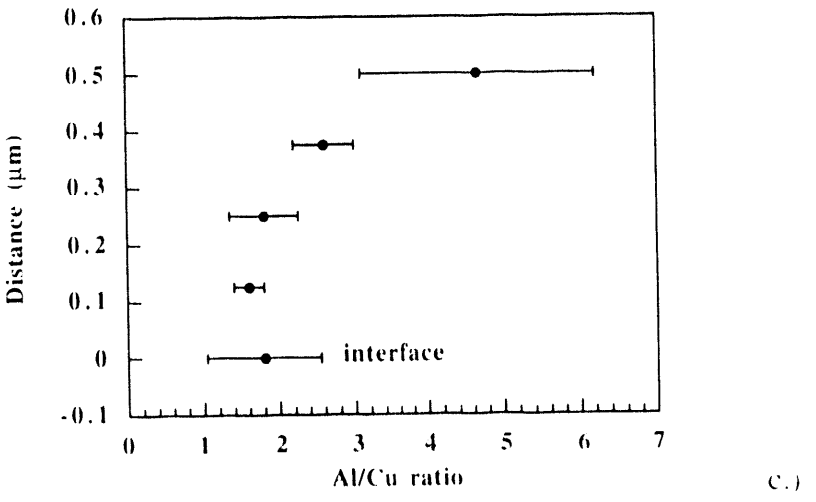


Figure 3.--Auger sputter profiles for a.) degreased, b.) de-oxidized, and c.) hydrotalcite coated Al 2024-T3.



c.)

Figure 4.--Cross-sectional TEM micrographs of hydrotalcite coatings on a.) 1100 Al, b.) 2024-T3 Al, and c.) Cu profiled through 1100 Al de-oxidized in a bath containing Cu.

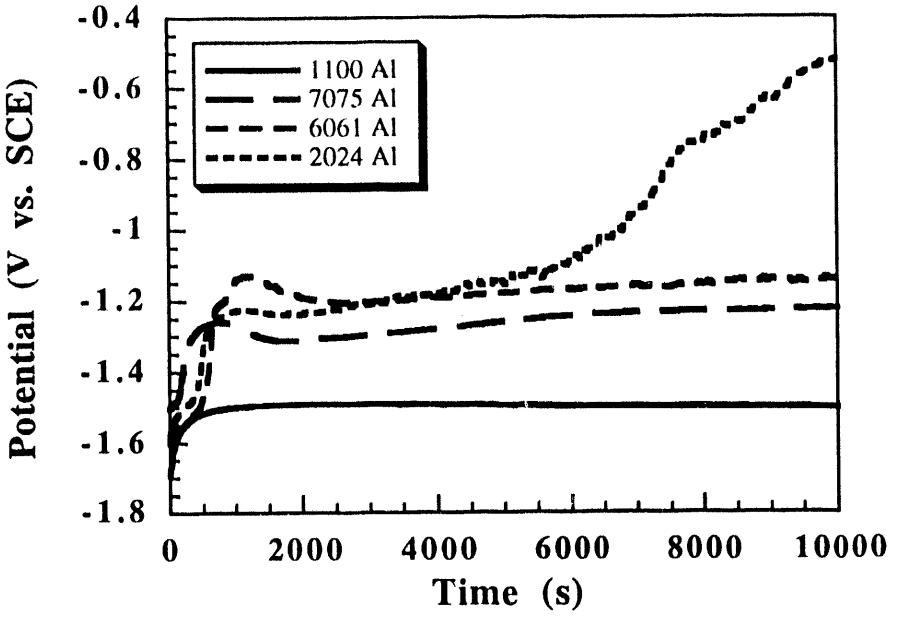


Figure 5.--Open circuit potential of Al alloys in 0.1 M Li_2CO_3/0.3 M LiOH coating bath.

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