LA-UR -88-3723

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TITLE ELECTRODEPOSITION OF ALUMINUM, ALUMINUM/MAGNESIUM ALLOYS, AND MAGNESIUM FROM ORGANOMETALLIC ELECTROLYTES

LA-UR--88-3723

DE89 003483

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SUBMITTED TO First International Congress: High-Tech-Materials and Finishing 1989
March 12-14, 1989
Berlin, West Germany

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ELECTRODEPOSITION OF ALUMINUM, ALUMINUM/MAGNESIUM ALLOYS, AND MAGNESIUM FROM ORGANOMETALLIC ELECTROLYTES

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ABSTRACT

The electrodeposition of aluminum, magnesium, and the combination of these metals from nonaqueous media is discussed. Plating baths for depositing Al/Mg alloys or for plating essentially pure Mg were developed. These solutions contain alkali metal fluoride or quaternary ammonium halide/aluminum alkyl complexes and dialkyl magnesium dissolved in aromatic hydrocarbons. Alloy deposits over the whole composition range can be plated from these solutions by varying the relative quantities of the aluminum and magnesium alkyls and by changing the bath-operating parameters.

INTRODUCTION

The active metals of most interest for electroplating are aluminum, magnesium, beryllium, and titanium. The deposits would have applications not only for functional and decorative coatings, but also for fabrication of lightweight, high-strength structures of high value such as space hardware. These metals cannot be plated from aqueous solutions because the hydrogen ions of the water are preferentially reduced over the active metal ions. Attempts to plate the active metals from aprotic solvent solutions have been made since the beginning of this century. Of the four metals mentioned above, only aluminum plating has been successfully reduced to industrial practice.

Aluminum Electrodeposition

Aluminum can be electrodeposited from aluminum compounds complexed with alkali metal hydrides or halides dissolved in organic aprotic solvents. Plotnikov[1] in 1902 and again in the 1930s[2] successfully deposited aluminum from aluminum bromide/alkali metal halide complexes dissolved in aromatic solvents. Peled and Gileadi[3] and Capuano et al.[4] more recently reported their investigations of the aluminum bromide plating baths. The first practical aluminum plating bath was discovered by Couch and Brenner[5] in 1952. This bath contained aluminum chloride/lithium hydride or lithium-aluminum hydride complexes dissolved in diethyl ether. Spurred by interests of the aerospace industry for lightweight electroformed parts and for engineering coatings, the Brenner bath and modifications thereof were developed into pilot plant processes. Schmidt and Hess[6] used the hydride bath for electroforming 76-cm-diameter solar concentrator mirrors. Lai[7] modified the Brenner bath with a mixed anisol-ether solvent for electroforming hardened aluminum for hollow-core solar panels. Daenen et al.[8] discussed the electrodeposition of aluminum from hydride complexes dissolved in tetrahydrofuran. Ziegler and Lehmkuhl[9] in 1954 discovered a new class of aluminum-plating electrolyte based on trialkyl aluminum/alkali metal fluoride or quaternary ammonium halide complexes. Dötzer[10] in 1964 and Birkle and Stöger[11] in the early 1980s further developed the organoaluminum electrolytes into practical commercial processes. Suchentrunk[12] reported on an industrial application of the organometallic plating system.

Magnesium Electrodeposition

Electrodeposition of magnesium and magnesium alloys from nonaqueous solutions has been investigated for over 70 years without yielding a practical method for commercial use. Most of the solutions from which Mg has been deposited, as they are reported in the literature, are based on Grignard reagents. Conner et al.[13] reported on magnesium plating from ether solutions containing magnesium halides, magnesium borohydride, and Grignard reagents. Their best coating was a magnesium alloy (90% Mg, 10% B) obtained from an ether solution of magnesium bromide and lithium borohydride. They reported organic matter contaminated poor quality Mg deposits.

from the Grignard-type baths. An aluminum alloy of 93% Al, 7% Mg was obtained by Conner from a bath containing magnesium bromide, aluminum bromide, and lithium aluminum hydride. However, the hardness of this alloy was appreciably lower than that of pure electrodeposited aluminum, suggesting perhaps that the deposit was not fully dense. Brenner and Sligh[14] reported on the deposition of magnesium from ether solutions of Gignard reagents and boranes. Their deposits were white, ductile, and contained at least 99% magnesium. Findl et al.[15] patented a process for magnesium electrodeposition based on Grignard compounds in ether solvent. The patent describes the continuous addition of an alkyl halide to the plating solution during electrodeposition at a sufficient rate to dissolve the sponge-like magnesium while not corroding the sound magnesium deposit. Lui et al.[16] attempted unsuccessfully to develop an Al/Mg alloy plating bath based on an aluminum chloride/lithium-aluminum hydride bath to which was added the Findl patented magnesium-plating solution. The mixed Al-Mg bath yielded a pure aluminum deposit with improved tensile strength and no evidence of codeposited magnesium.

We developed plating solutions based on the organometallic electrolytes for depositing essentially pure Mg and Mg/Al alloys spanning the total composition range.[17] The solutions contain trialkyl aluminum/potassium fluoride complexes and dialkyl magnesium dissolved in aromatic hydrocarbons.

EXPERIMENTAL

Development of Mg/Al Alloy Bath

In a previous publication[18] we reported the evaluation of the organometallic aluminum bath for electroforming applications. The electroformed deposits were of high purity and therefore exhibited a relatively low ultimate tensile strength of 65.5 MPa. Attempts to strengthen the deposit by dispersion hardening with codeposited fine particles were unsuccessful. We therefore explored the possibility of plating an alloy of aluminum from the organometallic solutions. We considered magnesium as an alloying constituent because magnesium alkyls are inexpensive and readily available commercial chemicals.

Because some of the organometallic compounds are pyrophoric in air and react violently with water, all operations were carried out under positive pressure with a continuous flow of dry nitrogen or argon. Most electrolysis experiments were conducted with bath volumes in the 100- to 500-ml range. The plating solutions were prepared from reagent-grade alkali metal fluorides or technical-grade tetramethyl ammonium chloride or fluoride, commercial triethyl aluminum, triisobutyl aluminum, 1.5 M diethyl magnesium in diethyl ether or 0.6 M dimethyl magnesium in diethyl ether Reagent-grade toluene was used as the solvent.

In trying to formulate a magnesium-plating bath, we first attempted to form complexes of magnesium alkyls and the alkali metal fluorides (for example $NaF \cdot 2\ [(C_2H_5)_2Mg]$ analogous to the Ziegler organoaluminum electrolytes. Complex formation between the alkyl magnesium and the metal fluorides did not occur. The alkali metal fluorides did not react with the alkyl magnesium in either diethyl or aromatic solvents at room or elevated temperature. The solutions showed no appreciable conductivity at 29 volt cell potential and no metal deposition occurred. When aluminum alkyls were slowly added to the above mixtures, a reaction probably formed the soluble alkyl aluminum/alkali metal fluoride complex. These solutions showed good conductivity and the deposits from them were either pure magnesium (>99 at.%) or alloys of aluminum and magnesium. Whether pure magnesium or alloys were deposited depended on the relative concentrations of the active species in the bath; that is on the alkyl magnesium and the alkyl aluminum and to a lesser extent on the operating parameters of the bath. In general, electrolytes containing mole ratios of aluminum alkyls to magnesium alkyls of 3.5 or less deposited essentially pure magnesium. The Al/Mg alloys were typically deposited from solutions containing aluminum alkyl to magnesium alkyl ratios of greater than 3.5. In all cases, the mole ratio of the aluminum alkyls to the alkali metal fluoride or quaternary ammonium halide was greater than 2.

The plating solutions can be prepared by combining the alkyl magnesium/diethyl ether solution with the alkyl aluminum and slowly heating the mixture to about 100°C to boil off the ether solvent. The toluene is then added to the solution followed by slow addition of the alkali metal fluoride. The solution is then heated and stirred to form the complex salts that are the conductive species of the electrolyte. An alternate bath preparation technique is to combine the alkyl magnesium with at least an equal molar quantity of the alkyl aluminum in the manner described above and separately form the alkyl aluminum-alkali metal fluoride (or quaternary ammonium halide) complex. The two solutions are then combined in the appropriate molar ratios to achieve the desired bath composition.

A typical bath for depositing pure magnesium was of the following composition:

Component	Mole Ratio
CsF	1
$(C_2H_5)_2$ Mg	2
$(C_2H_5)_3$ Al	4
iso$(C_4H_9)_3$ Al	2
Toluene	3

A 2.5 cm x 2.5 cm x 25 μm foil was electroformed in this solution at 1 A/dm^2 under moderate agitation at 40°C. The X-ray fluorescence spectroscopy and analysis done by inductively coupled plasma atomic-emission spectroscopy and mass spectroscopy showed the deposit to be greater than 99.5 at.% pure magnesium.

A typical bath for depositing a Mg/Al alloy contained the following:

Component	Mole Ratio
KF	1
$(C_2H_5)_2$ Mg	0.67
$(C_2H_5)_3$ Al	2.5
iso$(C_4H_9)_3$ Al	0.83
Toluene	1.5

A brass panel plated in this bath at 1 A/dm^2 (typical cell voltage was 1-5 volts) at 109°C produced a bright deposit of the approximate composition 50 at.% Mg/50 at.% as analyzed by x-ray fluorescence spectroscopy.

To determine the range of alloy composition that can be obtained from these solutions, we first prepared a bath that plated essentially pure magnesium. To this bath an aluminum electrolyte containing the NaF·2 $(C_2H_5)_3$ Al complex in toluene was added in increments and the composition of the resulting deposits was analyzed by x-ray spectroscopy after each addition. Figure 1 shows the x-ray spectra of these deposits as the composition shifts from an essentially pure Mg deposit (upper left) to one that is almost pure Al (lower right).

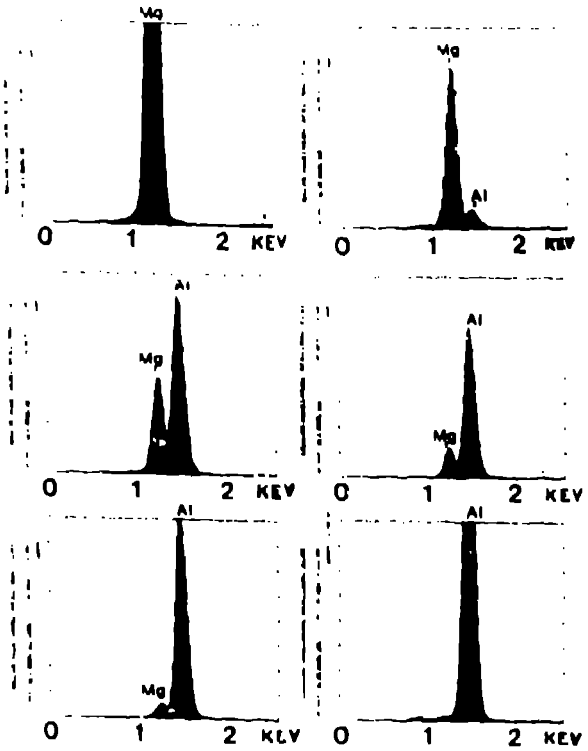

Fig. 1 - X-ray spectra of deposits from a magnesium bath with incremental additions of NaF·2 $(C_2H_5)_3$ Al.

Typical cell voltages were in the 1- to 5 volt range. The Mg content of the alloy generally increased with elevating the bath temperature. Anodes of magnesium and aluminum and inert anodes of gold plated copper or brass panels were used. Cathode and anode efficiencies have not been determined. The alloy deposits were generally smooth and bright in the 10% to 90% composition range of both metals. Outside these limits, the deposits remained smooth but were mat gray in color. The microhardness of a small number of deposits from these solutions plotted against their composition is shown in Fig. 2.

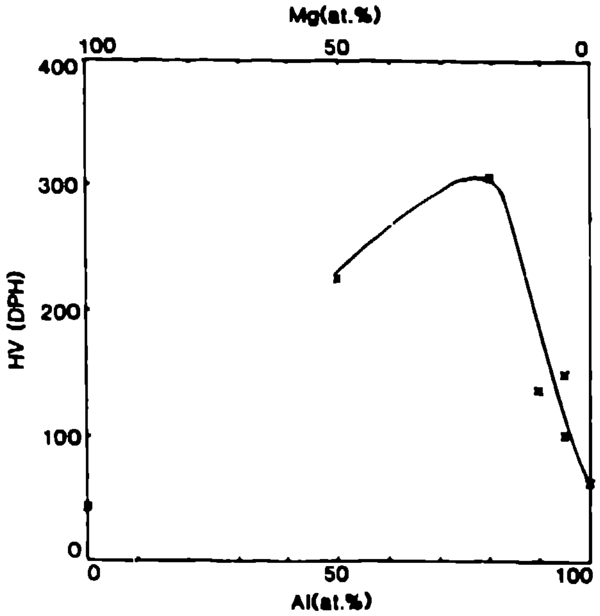

Fig. 2 - Microhardness of Mg, Al, and Mg/Al alloys electrodeposited from organometallic solutions.

A fivefold increase in deposit hardness over the pure deposits was observed at an alloy composition of $Al_{\sim 80}Mg_{\sim 20}$. The harder deposits suggest an increase in strength, and therefore the alloys should have advantages for electroforming applications.

DISCUSSION

The deposition of pure Mg and Mg/Al alloys from aluminum alkyl complexed solutions was surprising because the alkyl magnesium alkali metal fluoride complex could not be formed thermally. Dötzer[10] listed Mg among other organophilic elements that are anodically dissolved in $Al(C_2H_5)_3$ containing electrolytes; however, he found no appreciable codeposition of Mg with Al in experiments on Al electrorefining. Typically, the anode scum was richer in Mg than was the starting commercial aluminum anode material.

A closed-loop mechanism for the electrodissolution and deposition of aluminum in aluminum alkyl electrolytes, first proposed by Lehmkuhl and critically reviewed by Dötzer,[10] is shown in Fig. 3. At the anode, aluminum is dissolved by the alkyl radical according to the reaction:

$$\mathrm{Al} + 3\ (\mathrm{C_2H_5})^{\cdot} \rightarrow \mathrm{Al}\ (\mathrm{C_2H_5})_3. \qquad (1)$$

On the cathode surface, deposited sodium metal first chemically reduces aluminum from the aluminum alkyls according to the reaction

$$4\ \mathrm{Al}\ (\mathrm{C_2H_5})_3 + 3\ \mathrm{Na} \rightarrow \mathrm{Al} + 3\ \mathrm{Na}\ [\mathrm{Al}\ (\mathrm{C_2H_5})_4]. \qquad (2)$$

If one assumes the formation of the complex $\mathrm{Na[(C_2H_5)_2\ Mg\ F\ Mg\ (C_2H_5)_2]}$ an analogous cycle can be constructed for Mg electrodeposition (Fig. 4).

However, because we were not able to form the $\mathrm{NaF \cdot 2\ (C_2H_5)_2\ Mg}$ complex thermally as mentioned before, a different explanation for Mg deposition, particularly at the beginning of the electrolysis process, is required. Perhaps the alkali metal fluoride/magnesium alkyl complex is formed electrochemically by the cathode reaction of $\mathrm{(C_2H_5)_2\ Mg}$ and Na in baths containing both $\mathrm{(C_2H_5)_3\ Al}$ and $\mathrm{(C_2H_5)_2\ Mg}$ according to:

$$3\ \mathrm{Mg}\ (\mathrm{C_2H_5})_2 + 2\ \mathrm{Na} \rightarrow 2\ \mathrm{Na}\ [\mathrm{Mg}\ (\mathrm{C_2H_5})_3] + \mathrm{Mg}. \qquad (3)$$

At the anode (in a freshly-mixed Al/Mg alkyl electrolyte with Mg anodes) the alkyl radical formed electrochemically as shown in Fig. 3 dissolves the Mg and the $\mathrm{Al\ (C_2H_5)_2F}$ complex combines with the $\mathrm{Na[Mg\ (C_2H_5)_3]}$ to form the intermediate complex according to

$$\mathrm{Al}\ (\mathrm{C_2H_5})_2\mathrm{F} + \mathrm{Na[Mg}\ (\mathrm{C_2H_5})_3] \rightarrow \mathrm{Na}\ [(\mathrm{C_2H_5})_3\ \mathrm{Al\ F\ Mg}\ (\mathrm{C_2H_5})_2]. \qquad (4)$$

If this mechanism is valid, the complex $\mathrm{Na[(C_2H_5)_2\ Mg\ F\ Mg\ (C_2H_5)_2]}$ would eventually form as the plating solution is electrolyzed.

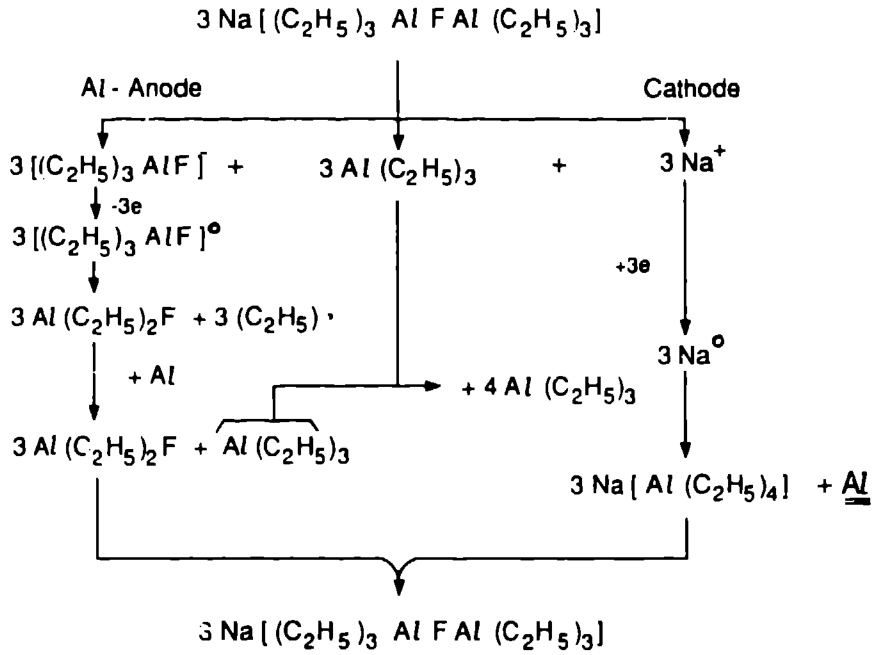

Fig. 3 - Lehmkuhl proposes closed-loop mechanism for electrodissolution and deposition of aluminum from aluminum alkyl electrolytes.

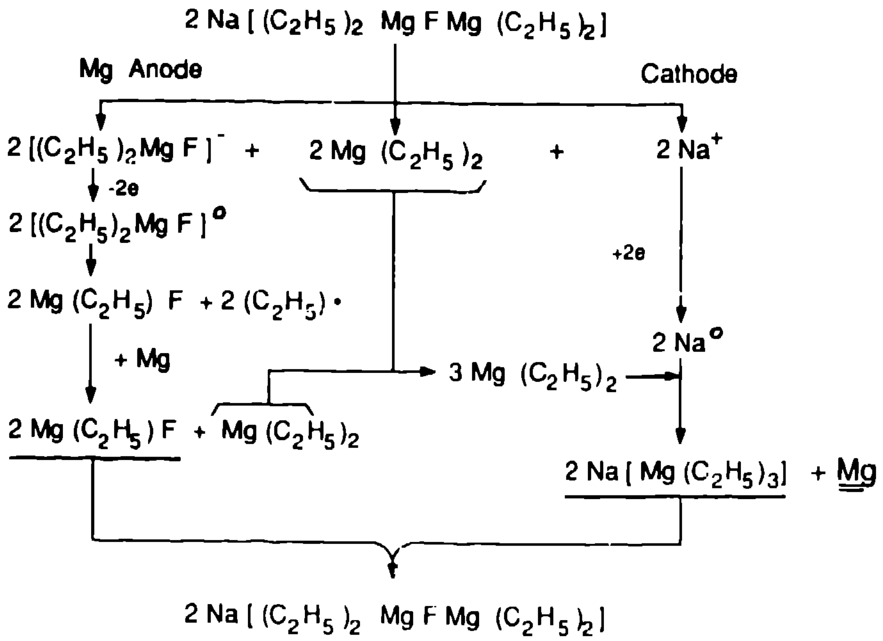

Fig. 4 - Possible mechanism for the reduction and oxidation of Mg in organometallic electrolytes.

The magnesium and aluminum/magnesium alloy-plating processes described here were based on one small scale laboratory evaluation and require further development before they can be proved commercially feasible. If proved practical, these processes should find applications for electroforming of lightweight components and for engineering coating applications.

SUMMARY

1. Solutions for electroplating sound deposits of essentially pure magnesium and alloys of magnesium/aluminum of a wide composition range have been developed. The solutions contain alkali metal fluoride (or quaternary ammonium halides), trialkyl aluminum and dialkyl magnesium.

2. Thin alloy deposits (<25 μm) between 10-90 at.% of either metal are typically fine grained and bright. Beyond these composition limits the deposit appearance is mat gray.

3. The hardness of the alloy deposits reaches a maximum of approximately 300 DPH at a composition of $Al_{\sim 80}Mg_{\sim 20}$.

4. A mechanism for the electrochemical formation of the alkali metal fluoride/alkyl magnesium complex and for the deposition or codeposition of Mg is suggested.

ACKNOWLEDGEMENTS

The author wishes to thank A. Jim Gray and Charles Javorsky for the metallography work. Thanks are also due to Maria J. Armijo for typing the manuscript and to Elaine Pinkerton for editing it. This work was supported by the United States Department of Energy.

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