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ELECTRODEPOSITION OF ALUMINUM FROM
NONAQUEOUS SOLUTIONS

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the act of March 3, 1883, as amended (45 Stat. 467; 35 U. S. C. 45).

This invention relates to the electrodeposition of aluminum from nonaqueous solutions, and in particular to a hydride type aluminum plating bath.

Several different types of baths for electroplating aluminum have been developed in the past. However, it has not been possible up to the present, to build up plates of more than 0.002 inch thickness without the plates becoming nodular or treed. Studies of additions to these baths have not as yet produced any appreciable improvement. These prior art methods probably all worked on the same basic theory; aluminum halide reacts with another halide which may be a quaternary ammonium salt or an alkali salt to form a complex salt $RAlCl_4$. This salt probably ionizes to form $AlCl_4^-$ ions which are discharged at the cathode as aluminum. Besides the disadvantage of not being able to build up very thick deposits, these prior art methods have the added disadvantage of requiring very critical control.

It is the primary object of the present invention to develop a method for the electrodeposition of aluminum that will produce relatively thick and smooth deposits of aluminum.

Another object of the invention is to develop a bath that is simply controlled.

Another object of the invention is to provide a bath for the electrodeposition of aluminum that is stable over long periods of time.

Another object is to develop a bath that requires infrequent filtration.

Another object is to develop a bath for the electrodeposition of aluminum that has deposition rates of at least 0.001 inch per hour.

According to the present invention the bath consists of an ethereal solution of anhydrous aluminum chloride and a metallic hydride. The concentration of aluminum chloride can be varied from 1 to 4 molar, but optimum results are obtained with a 2 to 3 molar solution. A number of different ethers were tried as the solvent but the best results were obtained when ethyl ether was used.

Good deposits were obtained, however, when several other ethers were employed. The results obtained with the different ethers are compared in Table 1.

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Table 1

Ether Used	Current density for best deposit	Relative rating	Type of Deposit
Anisole (methyl-phenyl).....	0.5	good.....	White, ductile, smooth.
Ethyl (diethyl)....	0.5-5.0	excellent.....	White, ductile, smooth, coherent.
Phenetole (Ethyl-Phenyl).....	0.5	good.....	Do.
Ethyl N-Butyl.....	0.5-1.0	do.....	Gray, brittle, coherent.
Di-Phenyl.....	0.5	do.....	White, ductile, smooth.

In addition to the ethers listed in the table a mixture of ethyl and butyl ether gave satisfactory deposits. The ethyl ether was necessary to give the desired solubility of the lithium hydride.

The allowable current densities were rather low for all except ethyl ether. However, even though the range for ethyl ether is from 0.5 to 5 amperes per dm^2 , optimum results were obtained with densities of approximately 2 amperes per dm^2 . At this current density, deposit rates of from 0.025 mm. to 0.05 mm. per hour were obtained. Aluminum anodes are used and dissolve in the bath at about 100 percent efficiency.

Several metal hydrides were used but lithium hydride at concentrations of from 0.5 to 1 molar give the best results. Lithium aluminum hydride gave equally good results, but the hydride contained insoluble fractions which have to be filtered out before use. Freshly prepared aluminum hydride also gave good results, but after standing for some time it was found to be insoluble when added to the bath.

The bath as described above has several distinct advantages. One is that the plating solution does not require frequent filtration, since the impurities from the aluminum chloride and the small amount of anode slime developed settle to the bottom of the vessel and usually do not affect the depositions. If small amounts of moisture enter the bath it is easily rejuvenated by the addition of the desired metallic hydride. Secondly the plating solution is stable over long periods of time if moisture is excluded. A sample of the plating bath which had been hermetically sealed for eight months yielded deposits as good as those from a freshly prepared bath.

In efforts to improve the deposits obtained by the original solution, periodic reverse currents were applied during the entire plating operation. This produced considerable smoothing of the deposits. A higher current for a short period of time is passed during the anodic cycle, but the

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ampere minutes are less than in the cathodic cycle. Table No. 2 shows the relation between the plate and reverse currents for several different plating operations and shows the results obtained.

Table 2

Time of complete cycle	Time of—		Current Density, amp./dm. ²		Time Ratio, Plate/Reverse	Effective Plating Current, amp./dm. ²	Type of Deposit
	Plate	Reverse	Plate	Reverse			
23.....	20	3	3	10	7	1.3	Smooth matt.
46.....	40	6	3	12	7	1.3	Very smooth.
84.....	80	4	3	12	20	2.4	Do.
168.....	160	8	3	12	20	2.4	Do.

Several addition agents have been tested but BB' dichloroethyl ether has been found to be the only one to have a marked effect upon the deposit. The addition of a sufficient amount of BB' dichloroethyl ether to constitute 4 to 8 percent by volume of the bath caused considerable smoothing and greatly increased the Vickers hardness. The Vickers hardness obtained depended upon the plating procedures used; that is, whether or not periodic reverse currents were used or BB' dichloroethyl ether was added. When neither was used the Vickers hardness ranged from 37 to 47 depending upon the current density employed. These deposits were very ductile. When periodic reverse currents were used with an effective plating current of 2 amperes per dm.² the Vickers hardness was 67 and the deposits were slightly less ductile. When BB' dichloroethyl ether was added the Vickers hardness was 97 and the deposits were brittle.

The deposits obtained besides being white and very smooth showed no appreciable amounts of lithium when lithium hydride or lithium aluminum hydride was used in the bath. The deposits ranged in thickness up to 0.75 mm. or approximately 0.03 inch, which is considered to be a very thick plate. The time required for plating is comparatively short; the deposition rate being 0.025 mm. per hour. Deposition rates as high as 0.05 mm. per hour are practical when a thinner plate is desired.

It will be apparent that the embodiments shown are only exemplary and that various modifications can be made in construction and arrangement within the scope of our invention as defined in the appended claims.

We claim:

1. A process of electroplating that comprises electrodepositing aluminum from a bath consisting of a mixture of an ether selected from the group consisting of ethyl ether, ethyl n-butyl ether, a mixture of ethyl and butyl ethers, anisole, phenetole, and di-phenyl ether; a metal hydride at 0.5 to 1 molar selected from the group

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consisting of lithium hydride, lithium aluminum hydride and aluminum hydride; and anhydrous aluminum chloride at from 1 to 4 molar.

2. A process of electroplating that comprises electrodepositing aluminum from a bath consist-

ing of a mixture of an ether selected from the group consisting of ethyl ether, ethyl n-butyl ether, a mixture of ethyl and butyl ethers, anisole, phenetole, and di-phenyl ether; a metal hydride at 0.5 to 1 molar selected from the group consisting of lithium hydride, lithium aluminum hydride and aluminum hydride; and anhydrous aluminum chloride at from 1 to 4 molar, and at current densities of from 0.5 to 5 amperes per dm.².

3. The invention according to claim 2 in which BB' dichloroethyl ether is used as an addition agent to improve the smoothness and hardness of the plating.

4. The invention according to claim 1 in which periodic reverse currents are applied across the bath, the effective plating current being from 1 to 3 amperes per dm.².

5. A non-aqueous bath for use in the electrodeposition of aluminum comprising an ether selected from the group consisting of a mixture of ethyl and butyl ether, anisole, phenetole, ethyl n-butyl ether, di-phenyl ether and ethyl ether; a metal hydride at 0.5 to 1 molar selected from the group consisting of lithium hydride, lithium aluminum hydride and aluminum hydride; and anhydrous aluminum chloride at from 1 to 4 molar.

6. The invention according to claim 5 in which BB' dichloroethyl ether is used as an addition agent to improve the smoothness and hardness of the plating.

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