United States Patent [19]

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[54] **ELECTRODEPOSITING OF ALUMINUM**

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[58] **Field of Search** ..... 204/14 R, 14 N, 39

[56] **References Cited**

UNITED STATES PATENTS

2,651,608	9/1953	Brenner	204/14 N

OTHER PUBLICATIONS

Journal of the Electrochemical Society, June, 1952, Vol. 99, No. 6, pp. 234–244.

Plating, Sept., 1969, pp. 1027–1037.

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[57] **ABSTRACT**

A method and bath for electrodepositing aluminum directly onto metal without the necessity of activation of the surface thereof wherein the bath is a mixture of anhydrous aluminum chloride at from 4.25 molar to saturation, an ether, such as ethyl ether, and a metal hydride, such as lithium aluminum hydride. Also an agent for improvement of the throwing power, such as ferric chloride, can be used.

13 Claims, No Drawings

ELECTRODEPOSITING OF ALUMINUM

This invention relates to electroplating of aluminum from non-aqueous solutions and to a bath for this purpose.

Plating processes and solutions for electrodeposition of aluminum are known such as disclosed in Brenner et al. U.S. Pat. No. 2,651,608 upon which this invention is an improvement. The solution in Brenner includes anydrous aluminum chloride with 4 molar concentration as the maximum. There also is a discussion of the subject in the article entitled "A Hydride Bath for the Electrodeposition of Aluminum" by Couch and Brenner appearing in the *Journal of the Electrochemical Society*, Volume 99, No. 6, Pp. 234 to 244. The procedures described in said patent and literature were generally complex and involve using various substrate activation solutions which introduce deleterious contaminants into the plating solution so as to shorten the useful life thereof by decomposing (through chemical reaction) the relatively expensive hydride in the bath. These described procedures also required different activation procedures and/or activation solutions for each metal substrate and were generally not oriented for production purposes.

One of the objects of the invention is to provide a process and bath for producing usable deposits of aluminum on metal.

Another of the objects of the invention is to provide a bath that is usable for long periods of time without changing or deterioration.

In one aspect of the invention, the process includes plating from a non-aqueous bath having a mixture which includes anhydrous aluminum chloride in a much higher concentration than previously used. A molar concentration of at least 4.25 molar through saturation is efficacious with the optimum being between 4.25 to 4.50 molar. The bath also has an ether and a metal hydride as set forth hereafter. Ferric chloride or an equivalent iron source also can be added.

The ether preferably is ethyl ether but ethyl n-butyl ether, a mixture of ethyl and butyl ethers, anisole, phenetole, and di-phenyl ether also can be used.

The metal hydride preferably is lithium aluminum hydride but lithium hydride and aluminum hydride also can be used.

The articles can be plated without the complex surface activation of the prior art. The article can be degreased if needed and then anodically etched in the bath for ½ to 15 minutes at current densities of ½ to 10 amperes per dm^2. The plating can be carried out in an increased range of current density, such as 5 amps/sq ft. to over 100 amps/sq.ft.

Also ferric chloride or an equivalent source of iron can be added to the bath which will improve the throwing power of the aluminum plating solution.

The standard plating solution of Brenner U.S. Pat. No. 2,651,608 has a boiling point of 50° – 55°C. as compared to the increased concentration of aluminum chloride of the present invention which raises the boiling point to 60° – 65°C.

It has been found that at the high current density end of the plate, treeing is less for the present invention and better coverage is obtained at low current density. Barrel plated parts have been satisfactorily plated at an average current density of 5 amps/sq.ft.

Polarity also can be advantageously reversed.

The following are specific examples of procedures in a bath of the present invention.

EXAMPLE I

Plating Solution Composition

$AlCl_3$ 4.73 Moles/liter
$LiAlH_4$ 0.41 Moles/liter
$FeCl_3$ (anhydrous) 1 gram/liter
Ethyl ether solvent

Plating on Titanium

1. No pretreatment/activation; degrease only if necessary.
2. Anodic etch in bath (separate etch bath not recommended) at 10 amps/sq.ft. for 2–3 minutes (typically for 8 inches × 18 inches barrel loads).
3. Rapid current reversal to make parts cathodic.
4. Plate at 10 amps/sq.ft. with no restriction on current density.

EXAMPLE II

Plating Solution Composition

$AlCl_3$ 4.28 Moles/liter
$LiAlH_4$ 0.40 Moles/liter
Ethyl ether solvent

Plating on Carbon Steel

1. No pretreatment or activation; degrease, only if necessary; de-rust (using e.g. Actane 85, a commercially available rust remover, "Actane" being the trademark of Enthone, Inc., for its brand of an acid pickling compound), only if necessary, and dry.
2. Anodic etch in bath at 10 amps/sq.ft. for 4–6 minutes.
3. No current 4–6 minutes to permit removal by agitation of anodic byproducts.
4. Plate at 10 amps/sq.ft. with no restriction on current density.

EXAMPLE III

Plating Solution Composition

$AlCl_3$ 4.37 Moles/liter
$LiAlH_4$ 0.40 Moles/liter
Ethyl ether solvent

Plating on Stainless Steel

1. No pretreatment/activation; degrease only if necessary.
2. Anodic etch in bath (separate etch bath not recommended) at 10 amps/sq.ft. for 2–3 minutes (typically for 8 inches × 18 inches barrel loads).
3. Rapid current reversal to make parts cathodic.
4. Plate at 10 amps/sq.ft. with no restriction on current density.

Summarizing, the increased concentration of anhydrous aluminum chloride enables the use of simple, universal activation procedures for various metal substrates and, more importantly, permits substrate activation within the aluminum plating solution which eliminates contamination of the plating solution from external activation solutions.

The plating solution of the invention results in an extremely long use life and exhibits excellent regenerative properties; is insensitive to high impurity levels (e.g., in plating aluminum onto titanium, Brenner uses two plating baths such that the titanium impurity from

deplating is confined to one bath); the high aluminum chloride concentration minimizes "treeing" or excessive buildup at high current density areas; the reduced vapor pressure and increased boiling point of the higher concentration plating solution provide an additional safety feature; and an increased usable range of plating current density (5 amps/sq.ft.) Is attained.

d. A 2.0×2.0×8.0 inch tank filled with aluminum plating solution to the 6.0 inch level was used. An 1100 aluminum alloy sheet, 1.0×5.0 inch immersed in the plating solution was used with a carbon steel cathode, also 1.0×5.0 inch immersed in solution. All plating was performed at 20 amps/sq.ft. current density for 1 hour for all specimens in both baths.

BATH LIFE TABLE

CUMULATIVE No. of RUNS	OBSERVATIONS OF QUALITY OF ALUMINUM DEPOSIT BRENNER TYPE BATH	BATH OF PRESENT INVENTION
1	Good, ductile aluminum	Good, ductile aluminum
10	Good aluminum, but slightly gray at corners (high current density areas)	Good, ductile aluminum
16	aluminum deposit still acceptable but somewhat gray in appearance with dark gray coloration at corners	No visible change in aluminum quality
19	Good, ductile aluminum	No visible change in aluminum quality
24	Dark gray coloration at corners	No visible change in aluminum quality
25	Dark gray coloration at corners	Slight change in coloration (darkening) of aluminum deposit. Aluminum still acceptable; slightly brittle. Added 0.1 M $LiAlH_4$ prior to start of 26th run.
26	Deposit covered with vertical gray streaks, very brittle. Added 0.1 M $LiAlH_4$ prior to start of 27th run.	Good, ductile aluminum
27	Acceptable aluminum, definitely below quality of original deposit.	Good, ductile aluminum
30	Dark gray coloration at corners	No visible change in aluminum quality.
31	Deposit dark, brittle, added 0.1 M $LiAlH_4$ prior to start of 32nd run.	No visible change in aluminum quality.
32	Aluminum deposit improved, but still poor, still somewhat brittle.	No visible change in aluminum quality
33	Dark gray coloration at corners. Added 0.1 M $LiAlH_4$ prior to start of 34th run.	No visible change in aluminum quality
34	Aluminum deposit dark and brittle. Added o.1 M $LiAlH_4$ prior to start of 35th run.	Slight change in coloration of aluminum deposit. Aluminum still acceptable. Added 0.1 M $LiAlH_4$ prior to start of 35th run
35	Aluminum deposit still dark and brittle. Bath no longer corrected by hydride addition	Good, ductile aluminum

A comparison of bath life between a fresh Brenner type aluminum plating bath

a. 3.0 M $AlCl_3$ and 0.4 M $LiAlH_4$ dissolved in ethyl ether, and a fresh aluminum plating bath in accordance with the present invention

b. 4.3 M $AlCl_3$ and 0.4 M $LiAlH_4$ dissolved in ethyl ether was made, and the results thereof are tabulated hereafter:

c. A small quantity (400 ml.) of plating solution was utilized rather than a larger volume so that the effect of impurity levels on the quality of the electrodeposit would occur quickly.

It will be understood that various details of construction and arrangement of parts may be made without departing from the spirit of the invention except as defined in the appended claims.

What is claimed is:

1. The process of electroplating comprising the steps of plating aluminum from a non-aqueous plating bath comprising the steps of electrodepositing aluminum from a bath consisting of a mixture of anhydrous aluminum chloride at from 4.25 molar to saturation; and 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; and a metal hydride selected from the group consisting of lithium hydride, lithium aluminum hydride and aluminum hydride.

2. The process as claimed in claim **1** wherein the ether is ethyl ether and the metal hydride is lithium aluminum hydride.

3. The process as claimed in claim **1** wherein the current density is from 0.5 to 10 ampers per dm^2.

4. The process as claimed in claim **2** wherein the current density is from 0.5 to 10 ampers per dm^2.

5. The process as claimed in claim **3** wherein anhydrous iron chloride is added to improve the throwing power of the bath.

6. The process as claimed in claim **1** wherein periodic reverse currents are applied across the bath, the effective current being from 0.5 to 25 amperes per dm^2.

7. The process as claimed in claim **1** wherein the part to be plated is anodically etched.

8. The process as claimed in claim **7** wherein the etch is in the range of 10 amperes per square foot and 2 to 3 minutes.

9. The process as claimed in claim **1** wherein the anhydrous aluminum chloride is 4.50 molar.

10. A non-aqueous plating bath for plating aluminum by electrodeposition on bare metal without activation comprising anhydrous aluminum chloride at from 4.25 molar to saturation; 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; and a metal hydride selected from the group consisting of lithium hydride, lithium aluminum hydride and aluminum hydride.

11. The plating bath as claimed in claim **10** wherein the ether is ethyl ether and the metal hydride is lithium aluminum hydride.

12. The plating bath as claimed in claim **10** wherein anhydrous ferric chloride is added to improve the throwing power of the bath.

13. The process as claimed in claim **1** wherein the anhydrous aluminum chloride is from 4.25 to 4.50 molar.

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