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The Electrodeposition of Aluminum from a Solution of Aluminum Bromide in *N*,*N*-Dimethyl Aniline

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This paper will describe that metallic aluminum was deposited electrolytically from a solution of aluminum bromide in dimethyl aniline with a current efficiency of 95% or more under optimum conditions. The superposition of a sinusoidal alternating current (AC) on the electrolysis direct current (DC) affected the properties of coatings and the throwing power of solutions to a great extent. A smooth, white-bright, ductile, and adherent coating was obtained under such appropriate conditions as that the frequency of AC was 60 Hz, the AC to DC ratio of 2 to 3. Aluminum dissolved anodically, and it was deposited at the cathode. The freezing temperature-composition diagram indicated the occurrence of two stoichiometric molecular complexes, $AlBr_3 \cdot C_6H_5N(CH_3)_2$ and $AlBr_3 \cdot 2C_6H_5N(CH_3)_2$, and the former was isolated.

Aluminum has not been deposited electrolytically from any aqueous solutions, probably because of the preferential discharge of hydrogen ions. For that reason, the electrodeposition of the metal from organic solutions containing no hydrogen ion has attracted considerable attention during the last about 20 years. The history has been well reviewed in the papers of Brenner[1-3] and other authors.[4] Several baths for the electroplating have been proposed by various investigators, but most of the baths are easily deteriorated by moisture and/or are difficult to operate. Of these, the lithium-aluminum-hydride-type bath, which was developed by Brenner and his co-workers,[5] would probably be the most excellent one for commercial use at present. The bath, however, seems not to be entirely perfect, because the solvent, diethyl ether, is inflammable and the aluminum dissolved at the anode does not deposit at the cathode. In order to improve this type of bath, Ishibashi and his co-workers[6] have proposed the use of tetrahydrofuran instead of ether as the solvent.

A variety of organic solvents has been examined by various authors in the studies of the electrodeposition of aluminum as well as of other metals, but *N*,*N*-dimethyl aniline (DMA) seems never to have been referred to. The present paper will describe that metallic aluminum was electroplated from the solution of aluminum bromide in DMA with a current efficiency of 95% or more under optimum conditions. When an alternating current (AC) was superimposed on the direct current (DC) in the electrolysis, a bright, ductile, and adherent coating was obtained.

Though preliminary experiments showed that aluminum chloride could be used as an alternative to the bromide, the latter was here chosen simply because its anhydride can be more easily prepared.

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[1] D. E. Couch and A. Brenner, *J. Electrochem. Soc.*, **99**, 234 (1952).

[2] A. Brenner, *ibid.*, **106**, 148 (1959).

[3] Ed. by P. Delahay and C. W. Tobias, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 5, J. Wiley/Interscience, N. Y. (1967), p. 205.

[4] I. A. Menzies and D. B. Salt, *Trans. Inst. Metal Finish.*, **43**, 186 (1965).

[5] J. H. Conner and A. Brenner, *J. Electrochem. Soc.*, **103**, 657 (1956).

[6] N. Ishibashi, Y. Hanamura, M. Yoshio, and T. Seiyama, *Denki-Kagaku* (A Journal published by The Electrochemical Soc. of Japan), **37**, 73 (1969).

In an electrochemical sense, DMA seems to be a moderately active solvent, having in the molecule a nitrogen atom capable of coordinating with a solute. On account of this property, DMA and its related compounds are worthy of study as non-aqueous solvents in the electrodeposition of metals, particularly of metals that have never been electrodeposited from aqueous solutions.

Experimental

Aluminum Bromide. Its preparation and subsequent purification were carried out in an all-glass apparatus capable of evacuation. The bromide was synthesized by heating alminum turnings (99.5% pure) in a current of purified bromine vapor. The bromide thus formed, without being exposed to the air, was purified by successive sublimation through a series of vessels, and finally sealed off in glass ampules, each of which was fitted with a breakable joint for subsequent use *in vacuo*. Colorless and anhydrous aluminum bromide was thus obtained.

N,N-*Dimethyl Aniline.* Care was taken to remove aniline, monomethylaniline, and water from a commercial DMA. When mixed with a suitable amount of acetic anhydride, it was submitted to fractional distillation. After the removal of the remaining acetic anhydride by washing with water, and the removal of the water by standing over potassium hydroxide, the distillate was further distilled fractionally under reduced pressure of nitrogen in the presence of metallic sodium.

Electrolysis Cells, Ancillary Apparatus, and Procedures. The cells and the procedures used here for the electrolyses were virtually identical with those of Menzies and others.[4,7] In brief, care was taken so as to prevent the contamination of the solution with atmospheric oxygen and moisture during both the mixing of the constituents and the electrolysis. About 40 m*l* of the solution was used in each run. The quantity of electricity (60—200 coulombs usually) passed through an electrolysis cell was measured with a water coulometer when an DC only was applied. The superposition of a sinusoidal AC on the DC was carried out by the usual method. The currents over a frequency range of 20—2,000 Hz were supplied from an audio-frequency generator. The net quantity of electricity participating in the cathodic process at the cathode was calculated from the area of a wave in an oscillogram of the resultant electrolysis current. In the expression for the ratio between the amount of superimposed AC and that of DC, the former was described by a root mean-square value.

Preparation of Electrodes. An aluminum spiral ribbon was generally used as the anode; at its center a cathode was placed. The aluminum was 99.5% pure, containing Fe, Cu, and Si as the main impurities. When the anodic dissolution of aluminum was studied, an aluminum wire anode (99.999% pure) was used. They were cleaned before use with a sodium hydroxide solution, dil hydrochloric acid, water, and finally with methanol. As the cathode a copper plate or a platinum wire was mainly used; its widest surface area was about 2 cm^2. They were cleaned in a mixture of hydrochloric, nitric, and sulfuric acids, as recommended by Graham.[8]

The aluminum deposited at a cathode was determined in two ways. One was a volumetric method, while the other was the measurement of the volume of the hydrogen generated by the addition of 8N hydrochloric acid. These two methods always gave concordant results, within the limits of experimental errors, which was a support for the idea of the deposit being completely metallic.

Adherence of Coating to Base Metal. This was estimated simply on the basis of the number of times at which a specimen was bent at right angles with pincers until the coating showed signs of flaking.

Freezing Temperature-Composition Diagram for the Solution System. The freezing points were determined on the basis of the cooling curves. The successive dilution of a solution with DMA was carried out in the presence of dry nitrogen (1 atmospheric pressure) in a vessel equipped with a magnetic stirrer.

Preparation of 1 : 1 Molecular Complex. After the dissolution of aluminum bromide in excess amounts of DMA with the aid of gentle heating, the excess DMA was permitted to distill off. The residue was then distilled at a higher temperature and collected in ampules. All the operations were carried out under a reduced pressure of nitrogen.

Results and Discussion

Appearance of Solutions. *In vacuo* or in an atmosphere of dry nitrogen free from oxygen, a newly-prepared solution of aluminum bromide in DMA was colorless at any temperature lower than about 100°C and at any concentration. At an elevated temperature above 100°C, the solutions gradually developed a color between light yellow and reddish orange *in vacuo* or in nitrogen, except for a solution with an equimolar composition, which was colorless irrespective of the temperature. In the air, the solutions containing less than 50 mol% of bromide turned blue. Even in the absence of oxygen, sunlight or ultraviolet rays also turned the solution blue. Sato[9] has shown that the reaction of DMA with aluminum chloride *in vacuo* gives a blue solution, the electronic spectrum of which displays an absorption maximum at 600—610 $m\mu$, and that the maximum is the same as crystal violet in the same solvent gives. In the present case of an aluminum bromide-DMA solution that was colored by virtue of oxygen or

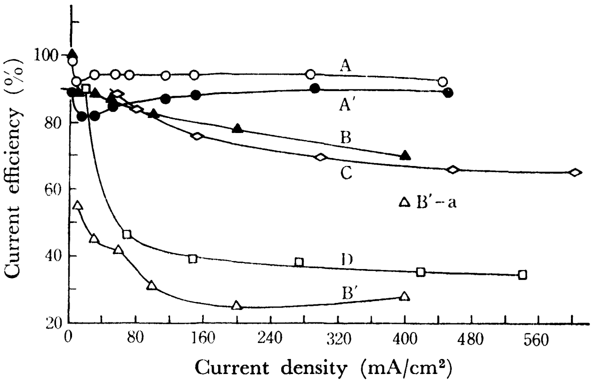

Fig. 1. Variation of cathode current efficiency with current density.

Curve	A	A′	B	B′	C	D
Concn. (mol%)	82.6	82.6	35.0	35.0	60.1	56.4
Temp. (°C)	120	150	120	80	120	120

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[7] I. A. Menzies and L. W. Owen, *Electrochimica Acta*, **11**, 251 (1966).

[8] A. K. Graham, *Trans. Amer. Electrochem. Soc.*, **52**, 289 (1927).

[9] H. Sato, This Bulletin, **38**, 1719 (1965).

ultraviolet rays, a maximum was also found at about 605 mμ. In the air, the solutions containing the bromide more than 50 mol% turned light brown; this was perhaps an alkaline color of crystal violet.

When electrolyzed, these solutions exhibited various colors, from blue to reddish violet, according to the experimental conditions. The coloring during electrolysis was partly attributed to unknown reactions at the anode.

Cathode Current Efficiency. The first run of electrolyses of freshly-prepared solutions occasionally yielded an unusually low current efficiency and a poorly adherent deposit. This is perhaps due to the trace amounts of water remaining in the solvent. The experimental datum of every first run was, therefore, discarded, or solutions were preliminarily electrolyzed for a while.

Figure 1 shows some examples of the effects of current density (CD) on the cathode current efficiency. At any concentration of aluminum bromide, the efficiency varied remarkably within a range of relatively low CDs; then it remained almost constant over a wide range of higher CDs. Again, the rise of the temperature decreased the efficiency rather slightly for concentrated solutions (curves A and A′), while it affected the efficiency for dilute solutions in the other direction (B and B′).

The variation in the efficiency with the concentration of aluminum bromide is illustrated in Fig. 2, which shows the case when the CD was 50 mA/cm^2 at 120°C. The efficiency varied unusually with the concentration, exhibiting maximum values of about 85 and 95% at concentrations around 35 and 65 mol% respectively. For the solution with an equimolar composition, the efficiency dropped unexpectedly, irrespective of the CD, to a value of about 50—60%. As is illustrated in Fig. 3, the curve for specific conductivity plotted against the composition of the solution also passed through a minimum at the equimolar composition, regardless of the temperature. It is of interest to note that the curve of Fig. 2 is, to some extent, similar in shape to that of Fig. 3; it is difficult at present to explain this.

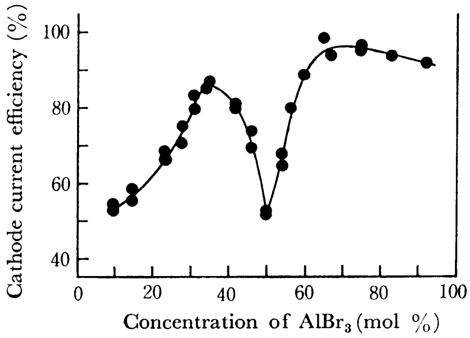

Fig. 2. Variation of cathode current efficiency with bath composition (120°C, 50 mA/cm^2).

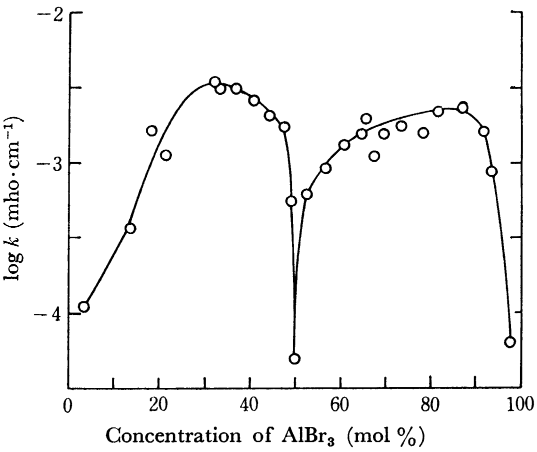

Fig. 3. Variation of specific conductivity (k) with composition at 110°C.

Improvement of the Properties of Coating by Superimposing AC. The deposits were metallic aluminum with no organic contaminants. They were, however, generally grey or sometimes black. Moreover, a nodular or dendritic growth of the deposit was often observed, particularly when the concentration of aluminum bromide was less than about 50 mol%. At higher concentrations these irregular growths diminished considerably, but were favored by high CDs. The adhesion of the coating to the substrate (copper or steel) was not very good, so pealing or blistering of the coating occasionally occurred, even when it was bent only once.

In order to improve the properties of the coating,

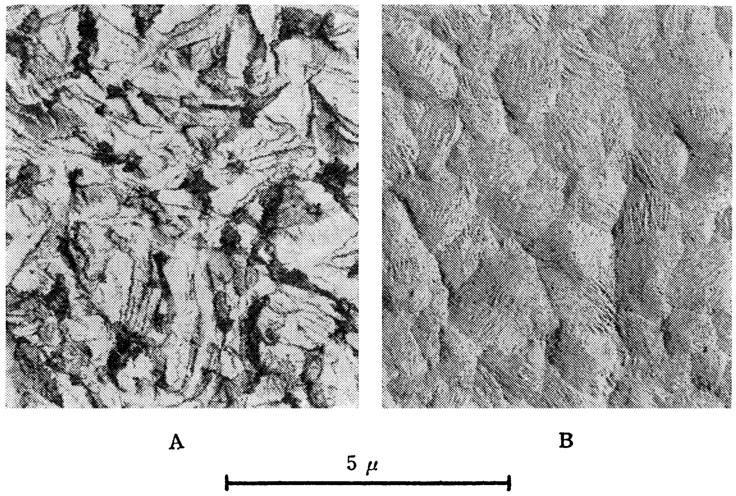

Fig. 4. Electron microphotograph (carbon replica) of surface of Al deposited (100 mA/cm^2, 58.5 mol%, 160°C).
A: DC only B: AC was superimposed (AC/DC = 3)

each of the following substances was added to the bath in various amounts of 10 to 1,500 mg/*l*. The attempt, however, was unsuccessful. The appearance and the adhesion were more inferior than ever. The tested substances were polyvinyl chloride, thiourea, sulfamic acid, benzoic acid, and sodium 2,7-dinaphthalen sulfonate. For the same purpose, a sinusoidal AC was superimposed on the DC for the electroplating. It affected the properties of coating to a great extent. The superposition, when the conditions were appropriate, yielded a smooth, white-bright, ductile and adherent coating, improving the throwing power of the bath, though the estimation of its extent was qualitative. Figure 4 (electron microphotographs) may be sufficient to illustrate that the superposition effectively smoothed the surface of the coating. Clean, white-bright electroplates as thick as 0.05 mm, which was not the maximum value possible, were easily obtained.

The frequency of a superimposed AC had appreciable effects on the properties of the coating and the throwing power of the bath. Generally, the favorable effects were observed at frequencies from roughly 60 to 200 Hz. At frequencies of 300 and 20 Hz, the coatings obtained were of a dull appearance and the throwing power was very poor. At frequencies above 300 Hz, grey coatings were obtained. At above 1,000 Hz, the coatings were black and less adherent than ever. The ratio of the amount of AC to that of DC was also one of the influential factors. The irregular growth was prevented when the ratio was more than 2. The current with an AC–DC ratio more than 4, however, generally yielded a poor cathode throw and a rough surface was deposited, particularly when the CD was high. The current efficiency decreased with an increase in the ratio. Some examples are shown in Fig. 5.

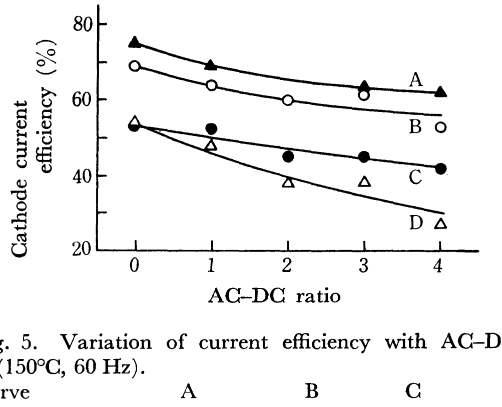

Fig. 5. Variation of current efficiency with AC–DC ratio (150°C, 60 Hz).

Curve	A	B	C	D
Concn. (mol %)	58.5	30.5	18.6	18.6
CD (mA/cm^2)	100	100	25	100

Anodic Behavior of Aluminum in the Solution. An aluminum anode dissolved electrolytically into the solution. Figure 6 shows the variation in the anodic current efficiency with anode CD. These efficiencies were computed for the formation of trivalent ions. At higher concentrations (above 55 mol%) of aluminum bromide, the efficiency was practically constant and was 100% over the whole range of CD observed; moreover, its change with the temperature was very small. Figure 7 shows the variation in the efficiency with the composition of the solution at 120°C and at a CD of 90—100 mA/cm^2. The efficiency decreased markedly as the concentration decreased below 50 mol%, and the solution adjacent to the anode turned blue or violet, seemingly because of the deposition of bromine.

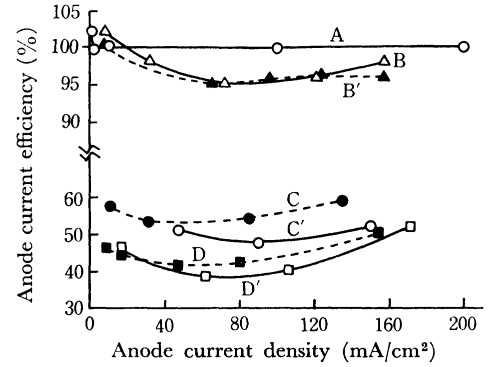

Fig. 6. Current efficiency for anodic dissolution of Al.

Curve	A	B	B′	C	C′	D	D′
Concn. (mol %)	92	48	48	35	35	22	22
Temp. (°C)	120	150	110	80	120	55	120

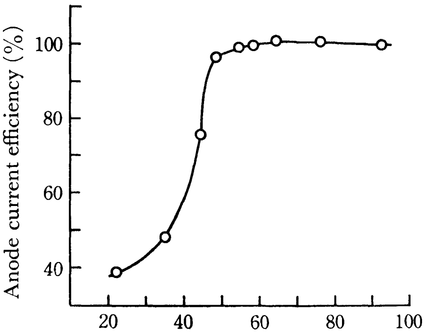

Fig. 7. Variation of anode current efficiency with composition (120°C, 90—100 mA/cm^2).

Conner and Brenner[5)] have reported that the aluminum dissolved at the anode did not deposit at the cathode in their Li-Al-hydride-type bath, probably because of the formation of a new ionic species. On the contrary, the following experimental facts suggested that the aluminum dissolved anodically could deposit at the cathode in the present bath. A solution of 6 m*l*, initially containing 68.5 mg of aluminum, was electrolyzed with an DC of 5 mA/cm^2 of CD for 72 hr; 198 mg of aluminum were thus deposited on the cathode. Similar results were obtained when an AC was superimposed.

Molecular Complexes between Aluminum Bromide and DMA. Figure 8 shows the freezing diagram of the system. An open circle represents the freezing point that was observed by cooling a solution from a temperature 10—20°C higher than the point. There were some cases in which the freezing point shifted slightly after the same solution had once been heated to about 150°C. The closed circles in the figure represent such cases. The curve connecting the open circles passes through one maximum and two minima; the latter are the freezing points of eutectic mixtures. The maximum at the equimolar composition suggests the occurrence of a molecular complex, the simplest formula of which is expected to be $AlBr_3 \cdot C_6H_5N(CH_3)_2$. Koblukow and

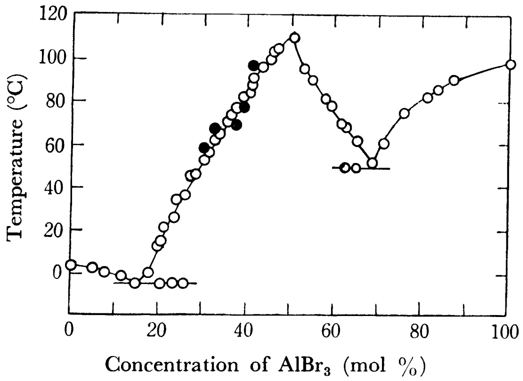

Fig. 8. Freezing temperature-composition diagram for $AlBr_3$-DMA system.

Ssachanow[10] have already reported a complex as being a dimeric molecule $Al_2Br_6\cdot 2C_6H_5N(CH_3)_2$ on the basis of their thermometric data. Its melting point (mp) was 95°C. On the other hand, the compound isolated by the present authors had a mp of 108—110°C. It seems likely, however, that these two compounds are the same. The difference in mp may be ascribable to the difference in purity between the two. The compound obtained here was colorless, crystalline, and somewhat hygroscopic; it was decomposed by water, but not so easily as aluminum bromide. It was colored blue by sunlight, but not by dry air. Found: Al, 6.92; Br, 61.4; C, 24.61; H, 3.52; N, 3.60%. Calcd for $AlBr_3\cdot C_6H_5N(CH_3)_2$: Al, 6.96; Br, 61.80; C, 24.77; H, 2.86; N, 3.61%. The apparent molecular weight of the complex in benzene was 402, while the calculated value for the monomeric molecule was 388.

The curve connecting the closed circles exhibits a discernible shoulder at the composition of about 33 mol%. This seems to indicate the presence of another complex, possibly $AlBr_3\cdot 2C_6H_5N(CH_3)_2$, though attempts at its isolation have not yet succeeded. Considering that the cathode-current efficiency exhibited a maximum around this composition, as may be seen in Fig. 2, this anticipated complex appears to be closely related to the behavior in electrolysis and to the conductivity of the solutions. An example is seen in Fig. 1. The curve B′ represents the current efficiency for a 35 mol% solution at 80°C; the solution had never been heated above this temperature. On the other hand, the point B′-a is for the same conditions except that the solution was once heated to 120°C. The difference in efficiency is remarkable. Again, the specific conductivity of any solution with a concentration of lower than 50 mol% was essentially changed and never returned to its initial value, after the solution had been submitted to a certain higher temperature. For example, the conductivity of the 33% solution was initially $10^{-3.7}$ $(\text{ohm.cm})^{-1}$ at 80°C; it finally became $10^{-2.6}$ at the same temperature after the solution had once been heated to 150°C.

The results described above are, of course, insufficient to establish the mechanism of the cathode reaction. The solution system displayed very intricate changes in conductivity as functions of the composition, the temperature, and the time of heating; the details will be reported at a later date. Throughout this study, the efficiencies were calculated for convenience on the basis of the reaction $Al^{3+}\rightarrow Al$. Considering the complicated change in the conductivity, together with that of the cathode-current efficiency, however, one can doubt whether the number of electrons, or the ionic species, participating in the cathode process would be the same throughout the whole range of aluminum-bromide concentrations. Further work, therefore, such as electrode-potential and transport-number measurements, will be required.

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10) I. Koblukow and A. Ssachanow, *Chem. Zentr.*, **1910 Bd. I**, 912 (1910).