研究ノート

Electrodeposition of Aluminum from the Hydride Bath Containing Aluminum Bromide

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Aluminum was successfully deposited from an ethereal bath containing aluminum chloride, lithium aluminum hydride and diethyl ether originally developed by Couch and Brenner¹⁾. As is discussed in the previous paper²⁾, one of the authors pointed out that different complex species from those in diethyl ether solvent bath were formed by using tetrahydrofuran (THF) as a solvent, and that the life of the bath could be considerably prolonged, because the aluminum dissolved from an anode could be deposited on a cathode.

In the present paper, electrochemical behavior of the bath containing aluminum bromide instead of aluminum chloride is studied. It was found that conductivity behavior and the best current densities range were quite differed from those of the bath containing aluminum chloride.

Procedure A solution of aluminum bromide was prepared by using aromatic hydrocarbon (benzene, chlorobenzene, o-dichlorobenzene, ethylbenzene, toluene, and xylene) containing 20 vol. % of THF in order to avoid a exothermic reaction with THF, and the electrolyte bath was prepared by adding a THF solution of lithium aluminum hydride to the solution of aluminum bromide. Conductivity measurements were carried out at 25.0°C and electrolysis were made at room temperature. Aluminum anode (1.5×3.0 cm²) and copper cathode (1.5×3.0 cm²) were used and there was no solution agitation.

Conductivity of the bath In the continuous variations method for determining the complex composition, specific conductivity was plotted against a mole fraction of lithium aluminum hydride at the constant total aluminum concentration, as shown in Fig. 1. The conductivity curve has two obvious inflection points at the AlBr₃/LiAlH₄ mole ratio of 3 and 1/3, and a point at the mole ratio of 1 is relatively clear in the system, AlBr₃-LiAlH₄-o-dichlorobenzene-THF, however no point is shown in benzene-THF mixed solvent. In the system, AlCl₃-LiAlH₄-THF, the clear points at the mole ratio of 3, 1 and 1/3 are shown³⁾. It is concluded that the current-carrying ion Li⁺AlHBr₃⁻ and non-conducting species AlH₃ are formed at the mole ratio of 1 and 1/3, respectively. The species formed at the mole ratio of 1 is considered

Table 1 Effect of solvents and current density on electroplating of Al at room temperature

solute : 0.5-0.6 M LiAlH₄, 0.5-0.6 M AlBr₃, mole ratio 1

solvents : 65 vol. % THF-35 vol. % aromatic hydrocarbon

○ silver-white deposit, △ silver-white deposit with dendrite at edges,
× black deposit

mixed solvents aromatic hydrocarbons		current density (mA/cm ²)							current efficiency*	
		10	30	50	80	100	150	200	anode(%)	cathode(%)
benzene	appearance	○	○	○	○	○	○	○	98-102	100-105
	mean bath voltage (V)	2.8	5.6	7.0	8.2	9.1	11.4	15.2		
o-dichlorobenzene	appearance	○	○	○	○	△	×	×	99-101	99-105
	mean bath voltage (V)	2.7	5.7	10.0	14.8	18.9				
ethyl benzene	appearance	○	○	○	○	○	△	×	95-100	101-103
	mean bath voltage (V)	2.8	5.0	8.5	14.5	18.2	27.0			
toluene	appearance	○	○	○	○	○	×	×	97	97
	mean bath voltage (V)	3.1	6.5	10.8	11.2	17.4				

* current efficiency was evaluated for 20 hours electrolysis at 10 mA/cm² and current efficiency range was obtained from five times electrolysis except for toluene-THF system.

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Fig. 1 Conductometric titrations of aluminum bromide with lithium aluminum hydride and vice versa in benzene (35 vol %)-THF solutions (○) and in o-dichlorobenzene (35 vol %)-THF solutions (△), under the condition of constant aluminum concentration, $[AlBr_3] + [LiAlH_4] = 0.100 \text{ mol/l}$, at 25.0°C

Fig. 2 Scanning electron microscope photograph of the surface of deposited aluminum bath composition; $[AlBr_3] = [LiAlH_4] = 0.500 \text{ mol/l}$ benzene (35 vol %)-THF condition of deposition;
a) 5 mA/cm^2 , 10sec (thickness $170 \text{ \AA}$), room temp.
b) 10 mA/cm^2 , 20min (thickness 4.1μ), room temp.

to play an important role for the deposition, because excellent deposits were obtained at the mole ratio 1-2.

Assuming that the dissociation constant of ion pair $(Li^+ AlH_2Br_2^-)$ is considerably lower than that of $Li^+ AlH_2Cl_2^-$, we account for the reason that the conductivity curve has no maximum at the mole ratio of 1. The dissociation constant of $Li^+ AlH_2Br_2^-$ in o-dichlorobenzene-THF is higher than that in benzene-THF because of high dielectric constant of o-dichlorobenzene. At the mole ratio of 1, precipitate of AlH_2I is quantitatively formed in THF by using aluminum iodide instead of aluminum bromide. The ease of separation of simple anions from ion pairs has the order; $AlH_2Cl_2^- > AlH_2Br_2^- \gg AlH_2I_2^-$, whereas no ionic species such as $AlH_2Cl_2^-$ and $AlH_2Br_2^-$, is shown in diethyl ether solvent because of precipitate of LiCl or $LiBr^{3),4)}$.

Electrodeposition of aluminum Excellent deposits were obtained from the bath containing an $AlBr_3/LiAlH_4$ mole ratio 1-2 and the hydrocarbon content less than 50 vol %. Electrolysis carried out at the mole ratio of 1 and at the hydrocarbon of 35 vol % were given in Table 1. The bath of the mole ratio of 3 or $1/3$ gave a good plating at lower current densities than 10 mA/cm^2 . A survey of plates made at different current densities revealed that the best current densities varied between $10\text{--}200 \text{ mA/cm}^2$ for benzene-THF mixed solvent and $10\text{--}100 \text{ mA/cm}^2$ for the other aromatic hydrocarbon-THF mixtures. The most marked indication in comparison with the deposits obtained from the $AlCl_3\text{--}LiAlH_4\text{--}THF$ bath was in plating quality in addition to high current densities applicable. Fig. 2 was taken with a scanning electron microscope. Fig. 2 a is the surface of $170 \text{ \AA}$ coatings. The surface has a fine-cylinder shape along with defects of rolled copper. Fig. 2 b is the typical features of the surface structure for the thicker coatings (4.1μ). Deposit showed the growth into ridges and crystal planes were obscure. The shape of the surface is little influenced by the current densities and by aromatic hydrocarbons. The smallness of the aluminum grain is considered to be the cause of brightness of the coatings. Conductivity of the bath ($AlBr_3$ 0.50M, $LiAlH_4$ 0.50M, THF 65 vol. %) is $3.3 \times 10^{-3} \text{ mho/cm}^2$ in o-dichlorobenzene-THF 2.4×10^{-3} in ethylbenzene-THF and 1.8×10^{-3} in benzene-THF, respectively. The conductivity of the bath, especially benzene-THF bath, is gradually decreased on standing the electrolyte for several days. This indicates that the decomposition of the solute occurs. The bath has a limited life. Comparison of the bath life of the two solvent systems indicates that the o-dichlorobenzene-THF and ethylbenzene-THF systems are preferable on the bath life. In the above solvent systems, the amounts of aluminum depositable was about equivalent to the amount of aluminum bromide used in the preparation of the bath.

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