Research Papers

Electrodeposition of Bright Al Coatings from Dimethylsulfone-$AlCl_3$ Baths with the Addition of Tetraethylenepentamine

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Electrodeposition of bright Al coatings from dimethylsulfone-$AlCl_3$ baths was demonstrated using tetraethylenepentamine (TEPA) as an additive. While the Al coatings electrodeposited from the bath without TEPA were lusterless, bright coatings with a mirror-like appearance showing high specular-reflectance were obtained in the presence of TEPA. Comparative examinations of the coatings revealed that the addition of TEPA changed the Al deposits from randomly-oriented, relatively-large crystals to (100)-oriented fine ones, and markedly decreased the surface roughness of the coatings. Cathodic polarization curves indicated that TEPA increased the overvoltage for the deposition of Al. Specific adsorption of TEPA on the Al deposits was considered to be the origin of the formation of the bright, leveled surface of the coatings.

Keywords : Brightener, Electroplating, Organic Solvents, Non-aqueous Solutions

1. Introduction

Aluminum (Al) coatings are employed in a wide range of industrial applications from construction materials to optoelectronic components, taking advantage of its excellent properties such as low density, high corrosion-resistance, high conductivity and high light-reflectivity. While most Al coatings are fabricated by hot-dipping or physical vapor deposition, electrodeposition of Al has attracted growing attention since complex-shaped objects can be coated evenly, the deposition rate is relatively high, and the thickness of the coatings can be easily controlled. Unlike other conventional metallic coatings, Al coatings cannot be electrodeposited from aqueous solutions. Electrodeposition of Al is, however, possible using non-aqueous media. Ionic liquids have been extensively studied as baths for the electrodeposition of Al in recent years[1)~8)], but the cost of the ionic liquids is high due to their synthetic complexity. Electrodeposition of Al from molecular organic solvents such as ethers and aromatic hydrocarbons has also been developed[9)], but they have drawbacks of high volatility and high combustibility. In contrast, dimethlysulfone (DMSO$_2$, **Fig. 1** a), molecular organic solvent, is much less expensive than ionic liquids, and more stable and thus easier to handle than the ethers and aromatic hydrocarbons. It has been demonstrated that dense, uniform Al coatings with a high corrosion-resistance can be electrodeposited from DMSO$_2$-$AlCl_3$ baths at ~110 ℃[10)~17)].

The Al coatings electrodeposited from the DMSO$_2$-$AlCl_3$ baths are, however, lusterless in most cases, losing their practical value in many applications. Since Al has high light-reflectivity, realization of bright, luster Al coatings will expand their applications to, e.g., decorative coatings and light reflection layers in optical devices such as LEDs. In general, the electrodeposition of bright coatings has been achieved by including certain additives, called brighteners, in the bath[18)], but no brightener has been found for the electrodeposition of Al from the DMSO$_2$-$AlCl_3$ baths, except $ZrCl_4$, which yields bright Al-Zr alloy coatings[15)]. It has been reported that bright Al coatings can be electrodeposited from ionic liquid baths with the addition of 1, 10-phenanthroline[8)] or toluene[3),6)]. Our preliminary experiments, however, showed that these additives did not work as brighteners in DMSO$_2$-$AlCl_3$ baths; the presence of a very small amount of 1, 10-phenanthroline in the bath strongly hindered the electrodeposition of Al and resulted in uneven deposits, while toluene did not affect the appearance of the Al coatings.

In this paper, we demonstrate the electrodeposition of bright Al coatings from DMSO$_2$-$AlCl_3$ baths with the addition of tetraethylenepentamine (TEPA, **Fig. 1** b), which we found acts as a brightener in this system. The effects of TEPA on the brightness, microstructure, and surface roughness of the electrodeposited Al coatings are reported, and the mechanism of the formation of the bright surface is discussed.

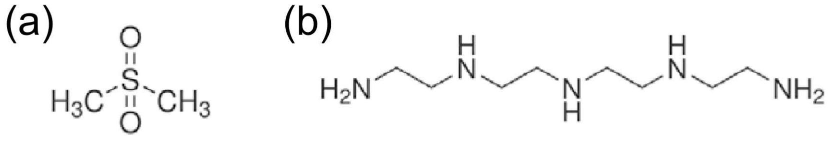

Fig. 1 Structural formulas of (a) dimethylsulfone and (b) tetraethylenepentamine.

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2. Experimental Section

2. 1 Electrodeposition

Preparation of the electrolytic bath and electrodeposition of Al were carried out in an Ar-filled glove box equipped with a circulation system. $DMSO_2$ (Tokyo Chemical Industry, 99%) and anhydrous $AlCl_3$ grains (Fluka, crystallized, 99%) were used as the solvent and Al source, respectively. TEPA (Tokyo Chemical Industry, 95%) was added to the electrolyte as an additive. The $DMSO_2$ was used after drying for 24 h at 60 ℃. $AlCl_3$ and TEPA were used as received. The molar ratio of $DMSO_2$ to $AlCl_3$ in the electrolyte was 10 : 2. The content of TEPA in the electrolyte was 0-0.2 mol with respect to 10 mol of $DMSO_2$. The electrical conductivity of the baths was measured with a conductivity meter (CM-30G, DKK-TOA Corporation). A glass vessel with a volume of 150 mL was used as the electrochemical cell. A copper plate (Nilaco, 99 %) and an Al plate (Nilaco, 99 %) were used as the substrate and counter electrode, respectively. Prior to the electrodeposition, the copper plate was polished with a SiC paper and then cleaned by sonication in ethanol. A part of the plate was covered with PTFE tape so that only a certain area (10 x 10 mm^2) would be exposed. Galvanostatic electrodeposition was performed with an electrochemical analyzer (ALS, model 660 C) at a current density of 40 mA cm^{-2} for 750 s, *i.e*, 30 C cm^{-2}. The temperature of the electrolyte was maintained at 110 ℃ by a thermostat. The electrolyte was stirred by a magnetic stirrer at 600 rpm during the electrochemical reactions. Assuming 100 % current efficiency, an Al layer with a thickness of about 10 μm was obtained under the deposition conditions. After the electrodeposition, the Al coating was washed with copious distilled water. The cathodic polarization curves were measured with Al wire immersed in the bath as the reference electrode by scanning from 0 V to negative potential at a rate of 10 mV s^{-1}.

2. 2 Characterization

Normal-incidence specular reflectance spectra for the electrodeposited coatings were measured using a multichannel photodetector (Otsuka electronics, MCPD-7700) coupled with an optical microscope (Nikon, Eclipse LV100). Spectra were taken from a 20 μm diameter spot using a 10x objective lens with a numerical aperture of 0.3 with reference to an Al mirror with a 50 nm MgF_2 coating (Sigma Koki Co., Ltd., TFA-25C05-20). The measured data were converted to absolute reflectance with the use of the simulated reflectance spectrum for the mirror. XRD patterns were taken by employing a diffractometer (Panalytical, X'Pert PRO-MPD) with Cu-Kα radiation. An FE-SEM (Hitachi, SU6600) was used to observe the surface morphology of the coatings. The roughness was measured by a surface texture measuring instrument with the nominal resolution of 0.4 nm in the z-direction (Surfcom 1400D, Tokyo Seimitsu). The parameters for the measurement were cutoff length of 0.8 mm and cutoff ratio of 300. The scanned length was 3.0 mm and the scan rate was 0.15 mm s^{-1}. The roughness was calculated based on ISO '97.

3. Results and Discussion

3. 1 Appearance and light reflectance of Al coatings

Al coatings electrodeposited from the $DMSO_2$-$AlCl_3$ baths without any additives usually look dull-white, i.e., lacking luster. However, as shown in **Fig. 2** comparing the appearance of the coatings electrodeposited from the baths without and with TEPA, the addition of TEPA to the bath changed the surface appearance of the resulting coating to a bright, mirror-like finish. The current efficiency was confirmed to be over 90 % from the thickness of the Al coatings in both the cases. **Fig. 3** presents normal-incidence reflectance spectra of the coatings, showing the brightness more quantitatively. While the reflectance of the coating from the bath without TEPA is about 10 % over the visible light region, that of the coating with TEPA is as high as 65 % at 450 nm and 80 % at over 600 nm. Our previous study demonstrated that Al-Zr alloy coatings with a similar brightness could also be electrodeposited by the addition of $ZrCl_4$ to the bath[15]. The $ZrCl_4$ addition, however, gave the metallic luster only to the central part of the electrodeposited area; the parts near the edge of the deposited area, where the current density should be locally high, remained dull-white. In contrast, the Al coatings deposited with the addition of TEPA showed the luster over the entire area as shown in **Fig. 2**, indicating that TEPA acts as a brightener in a wider range of current density.

3. 2 Microstructure

Fig. 4 shows typical SEM images of the coatings deposited without and with TEPA. The coating deposited without TEPA (**Fig. 4** a) is composed of randomly-oriented, well-faceted Al crystal grains 1-5 μm in size, which make the coating surface

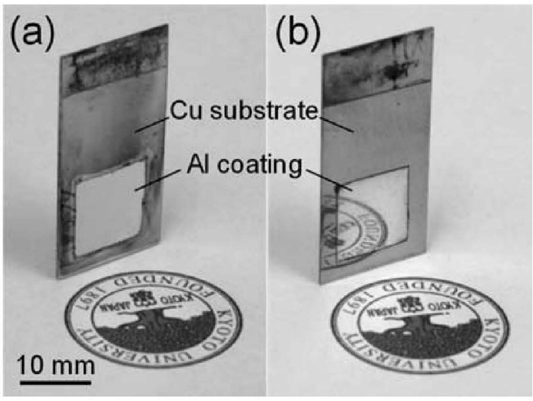

Fig. 2 Appearance of Al coatings electrodeposited on Cu substrates from $DMSO_2$-$AlCl_3$ bath (a) without and (b) with the presence of 100 mmol TEPA.

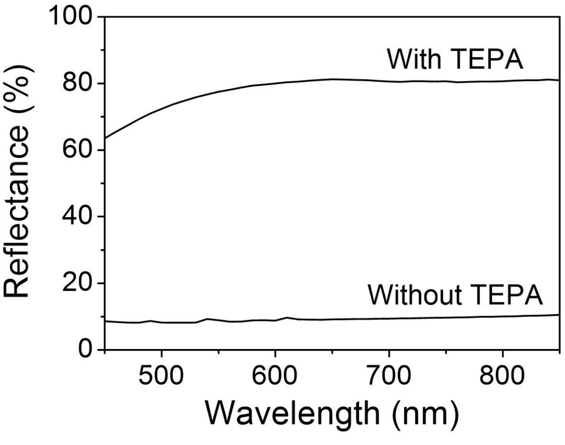

Fig. 3 Normal-incidence reflectance spectra of matte and bright Al coatings electrodeposited from $DMSO_2$-$AlCl_3$ baths without and with 100 mmol TEPA, respectively.

relatively rough. The addition of TEPA decreased the grain size of Al to 10-30 nm, forming a smooth, flat surface (**Fig. 4** b). This microstructural change is the origin of the difference in the reflectance and the appearance of the coatings: the coating without TEPA shows low specular reflectance and looks lusterless because the microscopically rough surface diffuses incident light in many different directions. In contrast, the smooth surface of the coating deposited with TEPA showed negligible light scattering, leading to the high specular reflection and the bright metallic luster. The decrease in the reflectance with decreasing wavelength observed in **Fig. 3** is because light with a shorter wavelength is more affected by small irregularities and thus scatters more markedly.

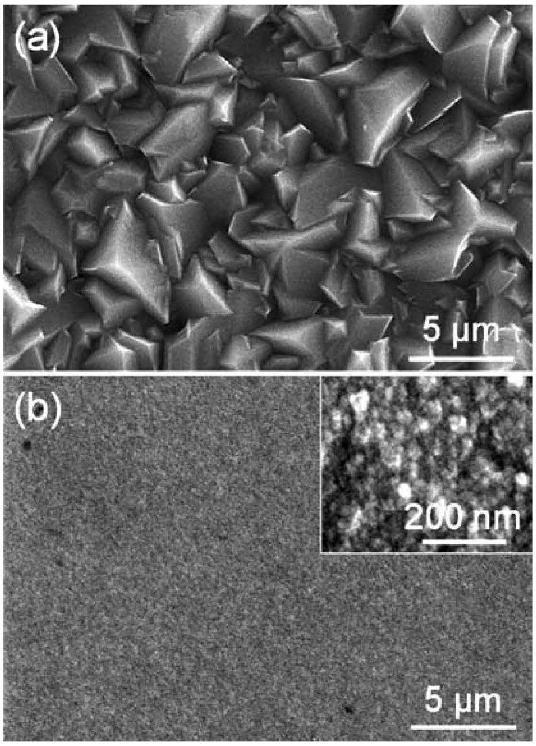

Fig. 4 Surface SEM images of (a) matte and (b) bright Al coatings electrodeposited from $DMSO_2$-$AlCl_3$ baths without and with 100 mmol TEPA, respectively.

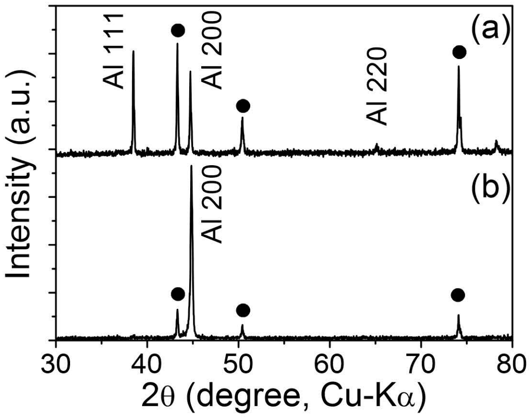

Fig. 5 XRD patterns of (a) matte and (b) bright Al coatings electrodeposited from $DMSO_2$-$AlCl_3$ baths without and with the presence of 100 mmol TEPA, respectively. Black circles denote diffraction peaks of Cu substrate.

3. 3 Crystal orientation

The addition of TEPA also affected the orientation of the deposited Al crystals. **Fig. 5** presents XRD patterns of the coatings deposited without and with TEPA. The pattern of the coating without TEPA (**Fig. 5** a) shows diffraction peaks of Al 111, Al 200 and Al 220, in addition to those of the Cu substrate, indicating that the coating is composed of randomly-oriented Al crystals, consistent with the SEM observation. On the other hand, the pattern of the coating deposited with TEPA (**Fig. 5** b) shows only the diffraction peak of Al 200, except for the reflections from the substrate, indicating that Al crystals with the (100) preferred orientation were deposited in the presence of TEPA. In many electrodeposition systems, it is known that the change in the preferred orientation is caused by preferential adsorption of foreign molecules[18]. The observed change in the crystal orientation therefore suggests that TEPA molecules preferentially adsorb onto a specific crystal plane of the Al crystals during the electrodeposition.

3. 4 Effect of TEPA concentration on roughness

The electrodeposition of Al was carried out from baths containing various amounts of TEPA to elucidate the appropriate range of TEPA content. **Fig. 6** shows the surface roughness, R_a, of the resulting Al coatings as a measure of the effect of TEPA. Bright Al coatings could be obtained in the range of TEPA content from 5 to 150 mmol. These bright coatings had a surface roughness smaller than ~0.06 μm, which is about one order of magnitude smaller than the value for the lusterless coating deposited without TEPA (~0.4 μm). When the TEPA content was more than 150 mmol, the surface of the coatings became rather rough or so-called burned. The examination with SEM and XRD confirmed that all the bright coatings obtained in this study shared the same aforementioned characteristics of being composed of fine Al crystals 10-30 nm in size and the (100) preferred orientation. The minimum roughness obtained in this study was 0.024 μm, which is much smaller than the value reported for a bright Al coating electrodeposited from an ionic liquid bath containing 1, 10-phenathroline as a brightener (R_a, = 0.12 μm)[8], indicating the better leveling ability of TEPA in the $DMSO_2$ based bath.

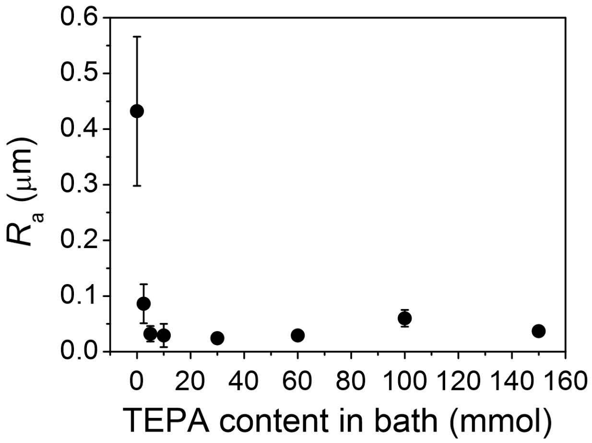

Fig. 6 Surface roughness (arithmetic mean roughness, R_a) of Al coatings electrodeposited from $DMSO_2$-$AlCl_3$ baths containing various amounts of TEPA.

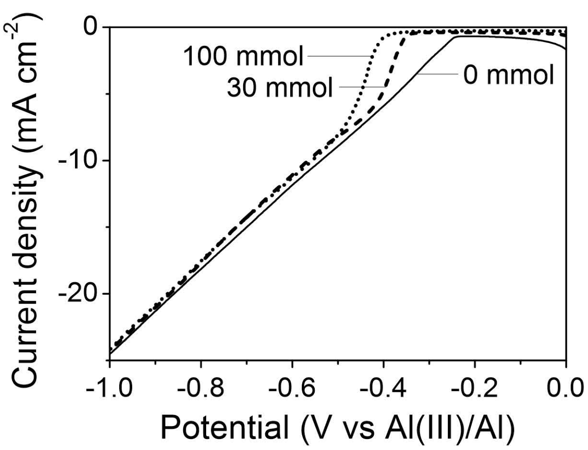

Fig. 7 Cathodic polarization curves for electrodeposition of Al in DMSO$_2$-AlCl$_3$ baths containing 0, 30, and 100 mmol TEPA.

3. 5 Mechanism of forming bright surface

In order to obtain better insight into the formation mechanism of the bright, flat surface by TEPA, cathodic polarization curves were measured in the baths with 0, 30, 100 mmol TEPA (**Fig. 7**). Clear differences among the polarization curves were observed in the low current density region ($<$5 mA cm^{-2}), although no significant difference was recognized in the higher current density region ($>$10 mA cm^{-2}), where the current densities increased linearly with lowering potential probably because IR drop over the electrolyte had a dominating influence on the polarization curves. It should be noted that the addition of TEPA only slightly decreased the conductivity of the bath from ~14 mS cm^{-1} without TEPA to ~13 mS cm^{-1} with 100 mmol TEPA at 110 ℃. In the low current density region, the polarization curves show that the overvoltage for the Al electrodeposition increases with increasing TEPA content, indicating that TEPA suppresses the Al electrodeposition. One might suspect that this suppression was caused by complex formation of Al ion with TEPA. However, the main cause of this suppression should not be the complex formation, but rather the absorption of TEPA onto the cathode surface, because TEPA acted effectively even at the very small content of 5 mmol (**Fig. 6**), which is 1/400 of the Al ion content in the bath. As described above, the adsorption of TEPA onto the cathode surface is also indicated from the change in the crystal orientation of the Al deposits. The formation of the bright surface of the Al coatings can therefore be explained by the same mechanism as the case of conventional aqueous electroplating with a typical brightener[18]: as the content of TEPA is low, TEPA molecules are preferentially adsorbed onto protruding parts of the cathode surface and thereby suppress the crystal growth of Al there, while the electrodeposition of Al occurs relatively more at concave parts, decreasing the surface irregularities. The refinement of the Al grains should be concomitantly caused by the adsorption of TEPA through the suppression of the crystal growth, also contributing to the formation of the smooth surface. A flat surface with a roughness smaller than the wavelength of the visible light looks bright and lustrous because incident light is specularly reflected without being scattered.

4. Conclusions

We demonstrated the electrodeposition of Al coatings with a bright, mirror-like appearance from DMSO$_2$-AlCl$_3$ baths by the addition of an organic additive, TEPA. The electrodeposition in the presence of TEPA yielded coatings composed of (100)-oriented fine Al crystals with a surface roughness smaller than ~0.06 μm. With the formation of the flat surface, the coatings showed a metallic luster with high reflectance of 65-80 % in the visible region. As is the case with typical brighteners employed in conventional aqueous electroplating, the preferential adsorption of TEPA onto the Al deposit was inferred to cause the formation of a leveled, bright surface. This realization of bright Al coatings largely expands the potential applications for electrodeposition of Al.

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