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Hull cell tests for evaluating the effects of polyethylene amines as brighteners in the electrodeposition of aluminum from dimethylsulfone-$AlCl_3$ baths

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ABSTRACT

Hull cell tests were carried out to examine a series of polyethylene amines to evaluate their abilities as brighteners in the electrodeposition of aluminum from a dimethylsulfone ($DMSO_2$)-$AlCl_3$ bath. The tests demonstrated the current density ranges that yielded bright, semi-bright, dull, burnt, and streaked Al deposits from the baths containing each polyethylene amine at a variety of concentrations. Among the amines examined in this study, triethylenetetramine (TETA) was found to be the most effective brightener, providing a bright Al deposit with the highest specular reflectance over a wide range of current densities. No correlation was found between the preferential crystal orientation of the Al and the brightness of the deposit, which along with the acquired scanning electron microscopy images, indicated that surface morphology was primarily responsible for the differences in brightness.

1. Introduction

Aluminum coatings are employed in a wide range of industrial applications from construction materials to optoelectronic components, taking advantage of their excellent properties, including 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 is attracting 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 many other conventional metallic coatings, those consisting of Al metal cannot be obtained by electrodeposition from aqueous solutions. However, it has been shown to be possible using certain non-aqueous media such as molten salts [1,2], organic solvents [3], and ionic liquids [4–12]. Among these, dimethlysulfone ($DMSO_2$), a molecular organic solvent, has the advantages of being much cheaper than ionic liquids, and more stable and thus easier to handle than the other organic baths such as ethers and aromatic hydrocarbons [3]. In $DMSO_2$-$AlCl_3$ electrolytes, there are two main soluble Al species, namely $AlCl_4^-$ and $Al(DMSO_2)_3^{3+}$, formed according to the following reaction [13]:

$$4AlCl_3 + 3DMSO_2 \rightarrow Al(DMSO_2)_3^{3+} + 3AlCl_4^-$$

The electrodeposition of Al can occur from the solvated cation, $Al(DMSO_2)_3^{3+}$, whereas the reduction of $AlCl_4^-$ is not observed within the electrochemical window of the electrolytes. 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 °C [14–22].

However, Al coatings electrodeposited from $DMSO_2$-$AlCl_3$ baths are lusterless in most cases, losing their practical value for many applications. As Al has high light reflectivity, realization of bright, lustrous Al coatings would expand their potential applications to, for example, decorative coatings and light reflection layers in optical devices such as LEDs. In general, the electrodeposition of bright coatings is achieved by including certain additives, called brighteners, in the electroplating bath [23]. However, effective brighteners for use in the electrodeposition of Al from $DMSO_2$-$AlCl_3$ baths have not been well developed to date, with only $ZrCl_4$ [19] and tetraethylenepentamine [22] having been reported to work to any extent. It is known that bright Al coatings can be electrodeposited from ionic liquid baths with the addition of 1,10-phenanthroline [7], benzene [11], or toluene [8,9]. However, our preliminary experiments 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 strongly hindered the electrodeposition of Al, resulting in uneven deposits, while toluene did not affect the appearance of the Al coatings at all.

Previously, we found that tetraethylenepentamine ($NH_2(CH_2CH_2NH)_nH$, $n=4$, TEPA) worked as a brightener for the electrodeposition of Al in a $DMSO_2$-$AlCl_3$ bath [22]. This motivated

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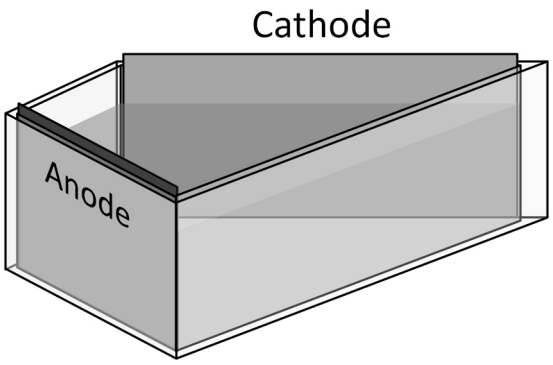

Fig. 1. Schematic view of Hull cell.

us to investigate other polyethylene amines. In the present study, we report on the use of a range of such compounds, from ethylenediamine (n = 1, EDA) to pentaethylenehexamine (n = 5, PEHA), with the aim of identifying a better brightener for the formation of brighter Al deposits at a wide range of current densities. Hull cell tests were used to estimate the current density range in which bright Al deposits could be obtained in the bath containing each amine. The Hull cell is a trapezoidal box of non-conducting material with one side at a 38° angle (Fig. 1). An anode is laid against the right angle side and a cathode panel is laid against the sloping side. When a current is passed through the solution contained in the cell, the current density along the sloping cathode varies in a known manner. In this way, the character of deposits over a wide range of current densities can be determined in a single experiment, and therefore, the Hull cell test is widely used for the control, evaluation, and development of various kinds of electrodeposition processes [24,25]. To date, no detailed Hull test results for Al electrodeposition from non-aqueous solutions have been published, although there was a brief mention in a paper by Abbott et al., where Hull cell tests were performed to optimize the conditions of the electrodeposition of Al from ionic liquids [10]. The deposition patterns shown in this paper will provide useful information for the comparison and assessment of baths for improved Al electroplating.

2. Experimental

Preparation of the electrolytic bath and the Hull cell tests were carried out in an Ar filled glove box equipped with a circulation system. $DMSO_2$ (99%, Tokyo Chemical Industry, Japan) and anhydrous $AlCl_3$ grains (Fluka, crystallized, 99%) were used as the solvent and Al source, respectively. EDA (n = 1, >98%, Wako Pure Chemical Industries, Ltd., Japan), diethylenetriamine (DETA, n = 2, >98%, Tokyo Chemical Industry, Japan), triethylenetetramine (TETA, n = 3, technical grade, Sigma–Aldrich), tetraethylenepentamine (TEPA, n = 4, >95%, Tokyo Chemical Industry, Japan), and PEHA (n = 5, technical grade, Sigma–Aldrich) were used as additives. The $DMSO_2$ was used after drying for 24 h at 60 °C. The water content of the $DMSO_2$ after the drying process was measured to be <10 ppm by a coulometric Karl-Fischer method (MKC-510 N; Kyoto Electronics Manufacturing Co., Ltd). $AlCl_3$ was used as received. The polyethylene amines were used after drying with molecular sieves (3A) for more than 12 h at room temperature. The molar ratio of $DMSO_2$ to $AlCl_3$ in the electrolyte was 10:2. The content of the additives in the electrolyte was adjusted in the range of 0–0.4 mol with respect to 10 mol of $DMSO_2$.

The Hull cell tests were conducted using a standard 267 mL Hull cell made of glass (Yamamoto-MS Co., Ltd). A Cu plate and an Al plate were used as the cathode and anode panels, respectively. Prior to the electrodeposition, the Cu plate was polished with SiC paper and then cleaned by sonication in ethanol. The bath was heated to 110 °C prior to the electrolysis by a ribbon heater wound round the sides of the cell. However, as the conductivity of the $DMSO_2$-$AlCl_3$ bath is relatively low (~14 mS cm^{-1} at 110 °C), and the current-to-volume ratio in the Hull cell is high, the bath temperature increases by more than 20 °C in the first 10 min after the start of the electrolysis through Joule heating. In order to suppress the temperature increase, the Hull cell was placed on a 30 °C cool plate (Scinics, CP-1200), where a Peltier device prevented the temperature from rising more than 10 °C. The bath was stirred by a reciprocating agitator (Kocour, Model A83) throughout the electrolysis procedure. The current for the electrolysis was supplied by a direct-current power source (Takasago, EX-750L2).

The Al deposits obtained by the Hull cell tests were characterized at a position of 3 cm from the bottom edge of the cathode panel at various horizontal distances. Normal incidence specular reflectance values were measured using a multichannel photodetector (MCPD-7700, Otsuka electronics) coupled with an optical microscope (Eclipse LV100, Nikon). The reflectance was captured from a 20 μm diameter spot using a 10× objective lens with a numerical aperture of 0.3, with reference to an Al mirror with a 50 nm MgF_2 coating (TFA-25C05-20, Sigma Koki Co., Ltd.). The acquired data were converted to absolute reflectance with the use of the simulated reflectance spectrum for the mirror. A scanning electron microscope (SEM, JSM-6510LV, JEOL) was used to observe the cross-sections and surface morphologies of the Al deposits. X-ray diffraction (XRD) patterns were obtained by employing a diffractometer (X'Pert PRO-MPD, Panalytical) with Cu-Kα radiation.

3. Results and Discussion

The Hull cell tests were conducted at a total current of 2 A for 600 s. Fig. 2 presents photographs of the cathode panels after the Hull cell tests for the baths containing no additives, TETA, and PEHA, showing typical appearances of the resulting Al deposits. It can be seen in most cases that an Al deposit with a relatively smooth surface was obtained in the middle area of the cathode panel, while a burnt section and one with streaks were observed near the left edge (high current density end) and right edge (low current density end) of the panel, respectively. The ranges where such deposits appeared depended on the type and quantity of the additive. The formation of the streaked deposit could be attributed to the following hypothesis: during the electrodeposition, a trace amount of a gas could be evolved at the cathode as a by-reaction, with these bubbles blocking the electrodeposition of Al as they move along the surface of the cathode, resulting in grooves or streaks in the deposit. Impurities such as water could be responsible for this gas evolution. It was sometimes observed that a part of the Al deposit near the left edge of the panel cracked and dislodged from the substrate (Figs. 2b and 2c). Such cracks only occurred in the area near the left edge of the panel, where the local current density and thus the thickness of the Al deposit were at their highest.

The brightness of the smooth Al deposit formed in the middle area of the cathode also depended on the additive. The deposit from the bath without additives appeared dull-white (Fig. 2a), with that from the bath with TETA looking brighter (Fig. 2b). Variation from dull-white to semi-bright was observed across the length of the deposit from the bath with PEHA (Fig. 2c). In order to quantitatively evaluate the brightness of the deposits, normal incidence reflectance at a wavelength of 550 nm was measured at various positions on the cathode panels. Fig. 3 presents the quantitative data that correspond to the deposits shown in Fig. 2. The dull-white deposit from the bath with no additive exhibited reflectances of about 20%, while the bright deposit from the bath with TETA gave values above 60%. The reflectance of the deposit from the