Electrodeposition of Aluminum from 1,3-Dimethyl-2-Imidazolidinone/$AlCl_3$ baths

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Abstract

This study investigated the use of novel organic solvent baths for the electrodeposition of aluminum at near-ambient temperatures. It was found that Al metal can be electrodeposited from baths that were composed of 1,3-dimethyl-2-imidazolidinone (DMI) and $AlCl_3$, with an $AlCl_3$ concentration greater than 50 mol%. IR spectroscopy indicated that $Al_2Cl_7^-$ ions were present in the baths that contained >50 mol% $AlCl_3$, where the electrodeposition of Al occurs from $Al_2Cl_7^-$ ion. The DMI/$AlCl_3$ baths with $AlCl_3$ concentrations between 59 and 64 mol% retained a single liquid phase without precipitation at 25 °C, and therefore, they can be used for Al electrodeposition near room temperature. Smooth Al films could be obtained by galvanostatic electrodeposition at 40 °C using a DMI/$AlCl_3$ bath with the addition of a trace amount of 1,10-phenanthroline.

Keywords: Electroplating, Electrodeposition, Organic solvent bath

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1. Introduction

Electrodeposition of aluminum (Al) at ambient temperatures has been widely investigated owing to a variety of potential applications that include uses in corrosion-resistant [1, 2] and decorative coatings [3], electrorefining processes [4, 5], and Al-ion batteries [6].

Because the electrodeposition of Al is not feasible in aqueous solutions, the use of non-aqueous media is required. Non-aqueous baths that have been developed for Al electrodeposition fall into three categories: inorganic molten salts, organic molten salts (i.e. ionic liquids), and molecular organic solvents [7]. Inorganic molten salt baths require a relatively high temperature (e.g., >140 °C for $AlCl_3$-NaCl-KCl baths [8]), may suffer from the volatilization of corrosive $AlCl_3$ gas, high energy consumption, and material limitations of the substrate and apparatus. In contrast, ionic liquid and organic solvent baths both allow Al electrodeposition at lower temperatures [7, 9-11]. Ionic liquids are attractive due to their low melting temperatures, low vapor pressures, and excellent chemical and thermal stabilities [10-12]. The main disadvantage of ionic liquids, as compared to organic solvents, is the high cost of the chemicals required to make the baths.

Organic solvent baths for Al electrodeposition are classified into three groups: ethers, aromatic hydrocarbons, and sulfones [7]. The etheric baths employ diethylether or tetrahydrofuran as the solvent and $AlCl_3$ combained with $LiAlH_4$ as the electroactive component [13-15]. The aromatic hydrocarbon baths consist of benzene, toluene, or xylene as the solvent and $AlBr_3$ or triethylaluminum as the electroactive component [7, 16-18]. While the Al electrodeposition processes using some of these baths have been commercialized [7], these baths often possess several key drawbacks, including high volatility and flammability, making handling of these baths challenging. Compared to etheric and aromatic baths, sulfonic baths have lower flammability and toxicity, making them safer and easier to handle. While the electrodeposition of smooth, dense Al coatings from dimethylsulfone ($DMSO_2$)/$AlCl_3$ baths has been previously reported [2, 5, 19-22], it was performed at a relatively high temperature, typically 110°C-130 °C (because the melting point of $DMSO_2$ is 109 °C).

In order to avoid the disadvantages mentioned above, we examined various organic solvent baths composed of $AlCl_3$ and a cheap organic solvent with a low melting point and low flammability to determine their proclivity towards electrodeposition of Al. The organic solvents examined include propylene carbonate, dimethylformamide, dimethylacetamide, trimethyl phosphate, triphenylphosphine, diethyl sulfate, and 1,3-dimethyl-2-imidazolidinone (DMI). These experiments revealed that Al can be electrodeposited from DMI/$AlCl_3$ baths. DMI is a non-ionic molecule with the structure shown in Fig. 1, and has a melting point of 8 °C, a high boiling point of 225 °C, and a flash point of 120 °C. In this paper, the conditions of Al electrodeposition from DMI/$AlCl_3$ baths are shown, and the mechanism is discussed. Furthermore, we demonstrate the electrodeposition of smooth Al films from a DMI/$AlCl_3$ bath with the addition of 1,10-phenanthroline [23] at 40 °C.

2. Experimental

2.1 Electrochemical experiments

Preparation of the electrolytic baths and electrochemical experiments were carried out in an argon-filled glove box (UNICO, UN-800F) equipped with a circulation system (UNICO, CM-200). The electrolytic baths were prepared by stepwise addition of anhydrous $AlCl_3$ grains (Fluka, crystallized, 99%; used as received) into DMI (Wako

Pure Chemical, 99%). DMI was used after drying with molecular sieves (3A) for >48 h. The water content of the DMI was determined to be <35 ppm by a coulometric Karl-Fischer method (MKC-510 N; Kyoto Electronics Manufacturing Co., Ltd). In order to remove impurities from the prepared bath, an Al wire was soaked in the bath for >24 h. The additive, 1,10-phenanthroline (Aldrich, 99%), was used after drying under reduced pressure at 60 °C for >24 h.

A 50 mL glass beaker with was used as an electrolytic cell, the temperature of which was controlled by a heater and thermostat (As-one, TJA-550). Cyclic voltammetry was carried out using a glassy carbon electrode and an Al plate as the working and counter electrodes, respectively. An Al wire directly soaked in the electrolytic bath was used as the reference electrode. The potential scan was started from the open circuit potential (0.3 V) to the cathodic direction at a rate of 50 mV s^{-1}. Potentiostatic and galvanostatic electrodeposition was performed on a Cu plate, which was previously 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 × 10 mm^2) would be exposed. During the electrodeposition process, the bath was agitated by a stirrer (Corning, PC-420D) at 150 rpm. The distance between the Cu plate and the Al counter electrode was 10 mm. The electrochemical experiments were carried out with an electrochemical analyzer (Hokuto Denko, HZ-5000).

2.2 Characterization

The surface morphology of the electrodeposited Al film was observed using a scanning electron microscope (SEM; JEOL, JSM-6519LV). The composition of the film was measured by an energy dispersive X-ray spectroscope (EDX) installed in the SEM.

The X-ray diffraction (XRD) pattern of the film was measured with a diffractometer (PANalytical, X'pert PRO-MPD) using the Cu-Kα line. The current efficiency for the electrodeposition of Al was obtained using inductively coupled plasma-atomic emission spectrometry (ICP-AES; SII Nano Technology, SPS 7800) to measure the amount of the electrodeposited Al film that was completely dissolved in a dilute hydrochloric acid, and then, the concentration of Al in the solution was determined by the ICP-AES.

Electrical conductivity and viscosity of the electrolytic baths were measured using a conductivity meter (Horiba, ES-51) and a tuning fork vibro viscometer (A&D, SV-10H), respectively. Infrared (IR) transmission spectra of the electrolytic baths were measured using a Fourier-transform IR spectrometer (FT-IR; Jasco, FT/IR-6200) at room temperature. This sample was prepared in the glove-box as a thin liquid film between a pair of polyethylene plates (Optics, 2.0 mm in thickness), and the edges of the plates were firmly sealed with a PTFE adhesive tape to prevent the liquid from reacting with air or moisture. The transmittance spectrum of the liquid film was obtained by dividing the measured spectrum by that of polyethylene.

3. Results and Discussion

3.1. Cyclic voltammetry and potentiostatic electrodeposition

Cyclic voltammetry was carried out for DMI/$AlCl_3$ baths with various $AlCl_3$ concentrations at 80 °C to explore the possibility of the electrodeposition of Al. Figure 2 shows voltammograms recorded in baths with 50.0 mol% and 54.5 mol% $AlCl_3$. A rise in the cathodic current was observed at –2 V on the negative scan of the voltammogram for the 50.0 mol% $AlCl_3$ bath (Fig. 2 (a)). An Al wire inserted into the bath was used as a reference electrode, meaning that, if the electrodeposition of Al was to occur, it should take place around 0 V. Because no significant current was observed at ~0 V, it is assumed that the electrodeposition of Al did not occur. If the Al electrodeposition had taken place during the negative scan, then the anodic current caused by the dissolution of Al should have been observed at around 0 V on the reverse positive scan. However, no significant current was observed for up to 1.5 V on the reverse scan, supporting that Al had not been electrodeposited on the negative scan. The cathodic current at below –2 V and the anodic current at over 1.5 V were ascribed to the decomposition of the bath. The voltammogram shapes for the DMI baths with <50 mol% $AlCl_3$ (not shown) were almost the same as for the bath with 50 mol% $AlCl_3$ that is shown in Fig 2 (a); namely, there was no sign of Al electrodeposition found in these baths. Conversely, the voltammograms for the 54.5 mol% $AlCl_3$ baths (Fig. 2 (b)) showed a rise in the cathodic current at 0 V on the negative scan, which is ascribable to the electrodeposition of Al. A second rise in the cathodic current was observed at around –2 V, which can be explained by the decomposition of the bath. On the reverse positive scan, the onset of the anodic current was observed at around 0 V, which should be due to the dissolution of Al that had been electrodeposited during the negative scan. Similar voltammograms were observed when the $AlCl_3$ concentration was in the range of 51 mol% to 60 mol%. These results of the cyclic voltammetry suggested that the electrodeposition of Al is possible in the DMI baths with an $AlCl_3$ concentration over 50 mol%.

In order to confirm that Al can be electrodeposited from the DMI/$AlCl_3$ baths with >50 mol% $AlCl_3$, potentiostatic electrodeposition was carried out at –0.4 V in the bath with 54.5 mol% $AlCl_3$ for 10 C cm^{-2} at 80 °C. The current density caused by the electrodeposition in these conditions was about 4.3 mA cm^{-2}. The electrodeposition yielded a gray film on a Cu substrate, as can be seen in Fig. 3. The SEM image of the deposit (Fig. 4) revealed that it was composed of grains that were 3-5 μm in size; the array of the grains reflects polishing marks on the substrate. The composition of the deposit, as determined by EDX, was 99.8% Al and 0.2% Cl, with the trace amount of Cl originating from the chloride ions in the bath. As shown in Fig. 5, the XRD pattern of the deposit only gave the diffraction peaks of Al metal, in addition to those of the Cu substrate, confirming that the deposit achieved by electrodeposition was elemental Al. We also conducted the electrodeposition using the DMI bath with only 16.7 mol% $AlCl_3$, confirming that no deposition was obtained from a bath with <50 mol% $AlCl_3$.

3.2. Speciation and mechanism

As described above, the Al electrodeposition was possible in the DMI/$AlCl_3$ baths only when the $AlCl_3$ concentration was higher than 50 mol%. This condition is the same in the baths of molten salts and ionic liquids, including NaCl/$AlCl_3$, [EMIm]Cl/$AlCl_3$, and [BPy]Cl/$AlCl_3$ systems [9]. Hence, the electrochemical reactions in the DMI/$AlCl_3$ baths are inferred to be similar to those in the molten salts and ionic liquid baths. It is known that, in molten salts or ionic liquids, Al ions exist in the form of $AlCl_4^-$ when the $AlCl_3$ concentration is lower than 50%, and $Al_2Cl_7^-$ arises alongside $AlCl_4^-$ when the $AlCl_3$ concentration is higher than 50% [24]. This is important because the electrodeposition of Al can only occur from $Al_2Cl_7^-$.

The Al ion species present in the DMI/$AlCl_3$ baths were assigned from the IR spectra by comparing them with the spectra of [BPy]Cl/$AlCl_3$ baths reported by Gale, *et al.* [24]. Figure 6 shows the IR spectra of the DMI/$AlCl_3$ baths. When the $AlCl_3$ concentration was 0 mol%, absorption peaks by DMI appeared at the wavenumbers of 326 cm^{-1} and 520 cm^{-1}. The DMI/$AlCl_3$ bath with 5 mol% $AlCl_3$ showed an additional absorption peak at 493 cm^{-1}. This absorption should be due to $AlCl_4^-$, because the absorption by $AlCl_4^-$ in the [BPy]Cl/$AlCl_3$ system appears at nearly the same wavenumber, 490 cm^{-1} [24]. When the $AlCl_3$ concentration was 60 mol%, the absorption peaks were detected at wavenumbers of 311 cm^{-1}, 330 cm^{-1}, 378 cm^{-1}, 390 cm^{-1}, and 433 cm^{-1}; also, a broad absorption was observed in a wide range of the wavenumber over 460 cm^{-1}. These wavenumbers agree with those of the absorption peaks by $Al_2Cl_7^-$ in the [BPy]Cl/$AlCl_3$ system [24], therefore indicating that $Al_2Cl_7^-$ also exists in the DMI/$AlCl_3$ bath. The absorption peaks by DMI and $AlCl_4^-$, which were supposed to appear at the wavenumbers of 326 cm^{-1}, 520 cm^{-1}, and 493 cm^{-1}, could not be clearly recognized in the spectrum of the bath with 60 mol% $AlCl_3$ because of the overlapping absorption by $Al_2Cl_7^-$.

The IR spectra indicated the presences of $AlCl_4^-$ in the DMI bath with 5 mol% $AlCl_3$ and $Al_2Cl_7^-$ with 60 mol% $AlCl_3$. From the results of the IR spectroscopy and the electrodeposition, the reactions occurring in the DMI/$AlCl_3$ baths are inferred to be as follows: when the $AlCl_3$ concentration is less than 50%, $AlCl_3$ dissolves to form $AlCl_4^-$ in the solution. Concurrently, the solvation of Al^{3+} ions by DMI molecules must occur because no source of Cl^- to form $AlCl_4^-$ exists other than $AlCl_3$ [20] (Reaction [1]). When the $AlCl_3$ concentration is higher than 50%, $Al_2Cl_7^-$ is generated according to Reaction [2]. While $AlCl_4^-$ and the Al^{3+} ions solvated by DMI molecules ($Al(DMI)_n^{3+}$) are not reducible, the electrodeposition of Al occurs from $Al_2Cl_7^-$ (Reaction [3]).

$$4AlCl_3 + n\ DMI \rightarrow 3AlCl_4^- + Al(DMI)_n^{3+} \quad [1]$$

$$AlCl_3 + AlCl_4^- \rightarrow Al_2Cl_7^- \quad [2]$$

$$4Al_2Cl_7^- + 3e^- \rightarrow Al + 7AlCl_4^- \quad [3]$$

This mechanism in the DMI/$AlCl_3$ system is analogous to that in ionic liquids, but different from the other organic solvent/$AlCl_3$ baths that have been successfully used for the electrodeposition of Al. In the conventional organic solvent/$AlCl_3$ systems, such as ethers/$AlCl_3$ and dimethyl sulfone ($DMSO_2$)/$AlCl_3$, the electrodeposition of Al is possible at a much lower concentration of $AlCl_3$. For example, the $AlCl_3$ concentration in the $DMSO_2$ baths is typically about 20 mol% [5, 20]. In these systems, the solvated Al^{3+} ions, or Al^{3+} complex ions coordinated by solvent molecules $Al(solvent)_n^{3+}$ are responsible for the electrodeposition of Al [20]. The Al^{3+} complex ions are reducible because of the weak coordination to Al^{3+} by the solvent molecules. In contrast, Al cannot be electrodeposited in many other organic solvent/$AlCl_3$ systems; for instance, it has been reported that the electrodeposition of Al was unsuccessful in propylene carbonate/$AlCl_3$ and dimethyl sulfoxide/$AlCl_3$ systems [20, 25]. The lack in viability of Al electrodeposition in these systems has been explained by the idea that the solvent molecules coordinate to Al^{3+} ions strongly and thereby prevent the Al^{3+} ions from electrochemically reducing to Al metal [20]. This is also the case with the DMI/$AlCl_3$ baths with <50 mol% $AlCl_3$. In the DMI/$AlCl_3$ system, however, we found that an increase in the $AlCl_3$ concentration beyond 50 mol% generates $Al_2Cl_7^-$, which is reducible to metallic Al. This finding leads to the expectation that Al electrodeposition is possible in other solvents, if $AlCl_3$ can be dissolved in the solvent at a concentration of over 50 mol%. We have examined propylene carbonate, dimethylformamide, dimethylacetamide, trimethyl phosphate, triphenylphosphine, and diethyl sulfate, but found that none of these solvents can dissolve $AlCl_3$ at over 50 mol%, and be used for Al electrodeposition.

3.3. Physicochemical properties

Cooling of the DMI/$AlCl_3$ baths results in the formation of a white precipitate from the solutions. The temperature at which the precipitation starts to occur depends on the concentration of $AlCl_3$. The lowest temperature above which the DMI/$AlCl_3$ bath can retain a single phase of a liquid solution was determined for the baths with various $AlCl_3$ concentrations (Fig. 7). In the range from 50 to 61.5 mol% $AlCl_3$, the temperature at which precipitation occurs drastically decreased with increasing $AlCl_3$ concentration. The baths with 61.5 mol% and 63.3 mol% $AlCl_3$ did not experience any precipitates even at the low temperature of –12 °C (the baths retained their liquid state at this temperature). $AlCl_3$ concentrations over 63.3 mol% experienced higher precipitation-inducing temperatures with increasing $AlCl_3$ concentration. The baths with $AlCl_3$ concentrations in the range of 59-64 mol% remained liquids with no precipitation at 25 °C, and can therefore be used as the baths for the Al electrodeposition at room temperature.

The electrical conductivity of the DMI/$AlCl_3$ bath with 60 mol% $AlCl_3$ was measured to be 1.7 mS cm^{-1} at 40 °C, which is about one tenth of the value reported for [EMIm]Cl/$AlCl_3$ bath with the same $AlCl_3$ concentration (~20 mS cm^{-1}) [26]. The viscosity of the same DMI/$AlCl_3$ bath was 35 cP at 40 °C, which is about two times higher than the value for the [EMIm]Cl/$AlCl_3$ bath at 25 °C (~16 cP) [27].

3.4. Al electrodeposition at near room temperature

Although we have demonstrated that Al can be electrodeposited from a DMI/$AlCl_3$ bath at 80 °C as described above, if smoother Al films can be formed at a lower temperature, the Al electrodeposition using the DMI/$AlCl_3$ bath will find a wider variety of applications. The electrodeposition of Al was therefore carried out at 40 °C using a DMI/$AlCl_3$ bath. Furthermore, 1,10-phenanthroline was added to the bath and examined for its ability as a leveler in this bath. It is known that 1,10-phenanthroline works as a leveler or brightener in the electrodeposition of Al from an ionic liquid bath [3]. The concentrations of $AlCl_3$ and 1,10-phenanthroline of the bath used in the present experiment were 60 mol% and 0.2 mol%, respectively. The electrodeposition was performed galvanostatically at the current density of 0.75 mA cm^{-2} for 10 C cm^{-2}. The cathode potential during the electrodeposition was measured to be about –0.3 V.

The electrodeposition at 40 °C yielded white or silver-gray films on the substrates in both cases with and without 1,10-phenanthroline (Fig. 8). SEM images of the electrodeposited films surfaces are shown in Fig. 9. The deposit from the bath without 1,10-phenanthroline was composed of grains with 3-5 μm in size (Fig. 9 (a)). Compared with the deposit obtained at 80 °C (Fig. 4), the deposit at 40 °C without 1,10-phenanthroline looked slightly coarser. With the addition of 1,10-phenanthroline to the bath, the size of the deposited grains decreased to ~1 μm, and thereby, a smoother surface was formed uniformly (Fig. 9 (b)). These results demonstrated that 1,10-phenanthroline works as a leveler in this bath and smooth Al films can be electrodeposited from the DMI/$AlCl_3$ bath even at 40 °C. The current efficiency for the electrodeposition of Al was about 85% in both cases with and without 1,10-phenanthroline.

When the electrodeposition was performed at a current density higher than 1 mA cm^{-2}, a smooth Al film was formed only at the central part of the electrodeposited area, and rough, black, so-called burnt deposits were generated at the parts near the edge of the electrodeposited area. The burnt area increased with increasing current density. Although the generation of the burnt deposit was suppressed by increasing temperature, the low current density of ~0.75 mA cm^{-2} was required to obtain the smooth film at the low temperature of 40 °C. Future work should focus on finding an additive or diluent [28, 29] to achieve the electrodeposition of a smooth Al film at a higher deposition rate at the low temperature in the DMI/$AlCl_3$ bath.

4. Conclusions

We found that Al can be electrodeposited from DMI/$AlCl_3$ baths. The cyclic voltammetry and potentiostatic electrodeposition revealed that the Al electrodeposition was possible only when the $AlCl_3$ concentration was higher than 50 mol%. The IR spectra indicated that the electrodeposition of Al occurred from $Al_2Cl_7^-$ ions. The DMI/$AlCl_3$ baths in the $AlCl_3$ concentration range of 59-64 mol% kept the liquid state without precipitation at 25 °C, and therefore, they can be used as the baths for the electrodeposition of Al at room temperature. Smooth Al film could be obtained by the electrodeposition at 40 °C using a DMI/$AlCl_3$ bath with the addition of 1,10-phenanthroline.

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Figure captions

Fig. 1 Structural formula of 1,3-Dimethyl-2-imidazolidinone (DMI).

Fig. 2 Cyclic voltammograms recorded at the carbon electrode in DMI/$AlCl_3$ baths with the $AlCl_3$ concentrations of (a) 50.0 mol% and (b) 54.5 mol% at 80 °C.

Fig. 3 Photograph of film obtained on a Cu substrate by potentiostatic electrodeposition in DMI/$AlCl_3$ bath with 54.5 mol% $AlCl_3$ at 80 °C.

Fig. 4 Surface SEM image of deposit obtained by potentiostatic electrodeposition in DMI/$AlCl_3$ bath with 54.5 mol% $AlCl_3$ at 80 °C.

Fig. 5 XRD pattern of deposit obtained on a Cu substrate by potentiostatic electrodeposition in DMI/$AlCl_3$ bath with 54.5 mol% $AlCl_3$ at 80 °C.

Fig. 6 IR spectra of DMI/$AlCl_3$ baths with $AlCl_3$ concentrations of (a) 0 mol%, (b) 5 mol%, and (c) 60 mol%. The gray bands indicates the positions of the absorption peaks by $AlCl_4^-$ and $Al_2Cl_7^-$ in [BPy]Cl/$AlCl_3$ baths [24].

Fig. 7 Diagram showing the lowest temperature above which DMI/$AlCl_3$ bath has a liquid state without precipitate.

Fig. 8 Photographs of Al films obtained by galvanostatic electrodeposition in DMI/$AlCl_3$ bath with 60 mol% $AlCl_3$ containing (a) 0 mol% and (b) 0.2 mol%

1,10-phenanthrorine at 40 °C.

Fig. 9 SEM images of Al films electrodeposited at 40 °C from a DMI/$AlCl_3$ bath with 60 mol% $AlCl_3$ containing (a) 0 mol% and (b) 0.2 mol% 1,10-phenanthroline.