Electroplating of Aluminum from Room Temperature Molten Salts Baths

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ABSTRACT

Room temperature molten salts baths of AlCl₃-BPC (1-butylpyridinium chloride) and AlCl₃-EMIC (1-ethyl-3-methylimidazinium chloride) were found as an electrolyte to obtain an excellent and high purity Al plating. These are inflammable and are easily operated at room temperature.

The properties of the molten salts and the plated Al film were investigated. The most suitable electrolyte composition was 67mol%AlCl₃-33mol%BPC or EMIC. The EMIC bath was better than the BPC bath as an Al plating electrolyte.

The Al plated carbon steel showed high corrosion resistivity.

A continuous Al plating process was developed.

INTRODUCTION

Electroplating of aluminum has been hoped as a surface treatment to improve a corrosion resistance of metals. Because the electroplating of aluminum from an aqueous solution is impossible, non aqueous solution must be used to carry out it. However, organic solvent systems are inflammable(1-4), and molten salt systems should be operated at high temperature(5). Therefore, an ambient temperature molten salt electrolyte has been examined to enable a low temperature and safe operation to plate aluminum(6,7).

EXPERIMENTAL

Molten salts baths were prepared by mixing of AlCl₃ and BPC or EMIC. Experimental were done in the dry box under N₂ atmosphere. A polarization curve was measured by using the Al, Cu, Pt electrodes. Counter electrode was 99.99% Al, and a reference electrode was an aluminum wire
in a 67mol%AlCl₃-33mol% BPC bath. Sweep rate was 50mV/sec. The salt spray test was done to evaluate a corrosion resistance of the Al plated sample. The solution was 5%NaCl and the temperature was 35°C. Surface and cross section of the sample was investigated by SEM.

RESULTS AND DISCUSSION

As an ambient temperature molten salt, a mixture of aluminum chloride and onium halide was investigated. The conductivity of the mixture is shown in Table 1. When imidazorium salts are used, high conductivity is obtained. However, when an alkyl group becomes large, the conductivity is close to that of pyridinium salt. In the case of ammonium salt that does not have a double bond, the conductivity is low. Then, a 1-butylpyridinium chloride (BPC) system and a 1-ethyl-3-methylimidazorium chloride (EMIC) system were selected for an Al plating bath.

Some characteristics for these AlCl₃-BPC systems are investigated. The results are shown in Fig. 1. Specific gravity became large with the AlCl₃ concentration. It was 1.34 for the 67mol% AlCl₃ bath. Viscosity and conductivity became low with the AlCl₃ concentration. When the viscosity decrease, the conductivity usually increases. However, in this case the conductivity decreased, although the viscosity decreased. This was considered to depend on a change of ionic species in the bath. Similarly, a change of some characteristics of EMIC system was also studied (Fig. 2). The specific gravity was larger than that of BPC system. The viscosity was smaller and the conductivity was larger than those for the BPC. Furthermore, melting point of EMIC system was lower than that of BPC system.

Cathodic polarization curves for various BPC baths are shown in Fig. 3. The potential, where a flow of a cathodic current begins, became noble when the AlCl₃ concentration goes up. The curves showed 2 peaks. A peak current of b increased with increasing the AlCl₃ concentration. Then, ionic species in the bath was investigated. Fig. 4 was obtained by the computer simulation from the equilibrium potential data and the equilibrium constants. In the acidic melt, a major Al ion is Al₂Cl₇⁻ and in the basic melt, a major Al ion is AlCl₄⁻. The AlCl₄⁻ ion decreases gradually with increasing the AlCl₃ concentration, while Al₂Cl₇⁻ ion increases suddenly from 50mol% AlCl₃. In Fig. 3, curve (1) has no peak b. Moreover, the peak current of b is going up with AlCl₃ concentration. Therefore, it was considered that Al₂Cl₇⁻ is reduced at the potential range of b. Moreover, the reaction of AlCl₄⁻ and 1-butylpyridinium cation may occur simultaneously at the range of a.

Next, anodic polarization curves were measured (Fig. 5). When the AlCl₃ concentration increased, a peak current of an anodic reaction decreased. A dissolution reaction of aluminum is an opposite reaction of the deposition. It was conceivable that the peak current became small with AlCl₃ concentration as an activity of AlCl₄⁻ becomes small with AlCl₃ concentration. Same tendency was obtained for the EMIC bath. Then, the reac-
tions of aluminum dissolusion and deposition were considered as follows.

(Cathodic reaction) \(4\text{Al}_{2}\text{Cl}_7^- + 3e \rightarrow \text{Al} + 7\text{AlCl}_4^-\) (1)
(Anodic reaction) \(\text{Al} + 7\text{AlCl}_4^- \rightarrow 4\text{Al}_2\text{Cl}_7^- + 2e^-\) (2)

From above facts, the Al plating bath composition was decided on 67mol\% AlCl\(_3\) baths.

First, maximum current densities of the plating and the dissolving were actually studied at various temperature as shown in Fig.6. The current densities go up together with temperature for both EMIC and BPC baths. The value for the EMIC was double of the BPC. It was consequently known that the EMIC bath is better than the BPC bath for the Al plating electrolyte. On the other hand, the dissolving current density is about 1/3 of the plating current density. Therefore, the positive electrode area needs 3 times of the negative electrode. SEM photographs of a surface and a cross section of the Al plating were observed. Very smooth coating was obtained.

The corrosion resistance of the Al plated sample was investigated by SST(Table 2). The substrate was a carbon steel precoated with Ni of 0.3um thickness. The chromate processing was not carried out. In the case of 5um plating thickness, 700 hours was required to rust occurrence. It was 1800h and 3000h at 10um and 30um, respectively. It was known that the aluminum plated material gives high corrosion resistance.

Next, a manufacturing process of the Al plating was examined. The flow chart is shown in Fig.7. The degreasing and also washing with acid were carried out. Both of the BPC melt and the EMIC melt strongly react with moisture. As the substrate is generally covered with oxides after drying, an adhesive Al plating can not be obtained. Then, the "activation" process was devised as follows. First, an anodic dissolution of the oxides in the BPC bath was attempted. In the case of Pt anode, a current was not observed up to 2.1V(Fig.8). In the case of stainless steel(SUS430), an anodic current flowed. Namely, a possibility of the dissolution of oxides was shown. The "activation" was studied at various electricities at anodic current of 0.4A/dm\(^2\) in the BPC bath(Fig.9). It was expected that the activation of surface completes over 1.3 coulombs/cm\(^2\). Relationship between the activation and the adheasion were studied(Fig.10). It was known that a sufficient adhesion for the Al plating is obtained, when the substrate is dissolved in 2 coulombs and then Al is plated on it. As a results, the industrialized Al plating line was completed. The Al plated coil and wire were made by the continuous plating line. The Al plated bolts were made by the barrel type line.

CONCLUSION

Room temperature molten salts of AlCl\(_3\)-BPC and AlCl\(_3\)-EMIC were investigated as an Al plating electrolyte. The results are as follows.

1) The most suitable electrolyte composition was 67mol\%AlCl\(_3\)-33mol\%BPC
2) In the case of the EMIC bath, the highest plating current density was 4 and 17 A/dm² at 25 and 100°C, respectively.
3) The anode surface area must need 3 times of the cathode.
4) The morphology of the Al plating was dense and smooth.
5) The high corrosion resistivity of the Al plated sample was proved.
6) A continuous Al plating process was developed. Consequently, many applications of the Al plating are expected.

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Fig. 1 Some characteristics for AlCl3-BPC baths.
- \( \bigcirc \): Specific gravity, 25°C, \( \bullet \): 30°C
- \( \triangle \): Specific conductivity, 25°C, \( \Delta \): 30°C
- \( \square \): Viscosity, 20°C, \( \blacksquare \): 30°C

Fig. 2 Some characteristics for AlCl3-EMIC baths.
- \( \bigcirc \): Specific gravity, 25°C
- \( \triangle \): Specific conductivity, 25°C
- \( \square \): Viscosity, 20°C
Fig. 3 Polarization curves for AlCl$_3$-BPC baths.
Sweep rate: 50 mV/s
(1) 50 mol% AlCl$_3$ - 50 mol% BPC
(2) 58 mol% AlCl$_3$ - 42 mol% BPC
(3) 60 mol% AlCl$_3$ - 40 mol% BPC
(4) 62 mol% AlCl$_3$ - 38 mol% BPC
(5) 64 mol% AlCl$_3$ - 36 mol% BPC
(6) 67 mol% AlCl$_3$ - 33 mol% BPC

Fig. 4 Mole fraction $N$ of the species in the melt at 60 °C as a function of AlCl$_3$ content.

---: Cl$^-$, -----: Al$_2$Cl$_7^-$, ------: AlCl$_4^-$
----: Al$_2$Cl$_6$, -----: AlCl$_3$, ----: BP$^+$
Fig. 5. Polarization curves for AlCl$_3$-BPC baths.

Sweep rate: 50 mV/s
(1) 58 mol% AlCl$_3$ - 42 mol% BPC
(2) 60 mol% AlCl$_3$ - 40 mol% BPC
(3) 62 mol% AlCl$_3$ - 38 mol% BPC
(4) 64 mol% AlCl$_3$ - 36 mol% BPC
(5) 66 mol% AlCl$_3$ - 34 mol% BPC
(6) 67 mol% AlCl$_3$ - 33 mol% BPC

Fig. 6. Maximum Al plating and Al dissolving current densities vs. temperatures.
Fig. 7 Flow chart of Al plating.

Fig. 8 Anodic polarization curves for 67 mol% AlCl₃-33 mol% BPC bath. (25°C)

(1) SUS 430
(2) Pt
Fig. 9 Rest potential after anodic polarization of various electricities at 0.4A dm$^{-2}$ in the BPC bath.

Fig. 10 Adhesion of Al plating for various activation conditions.
Table 1 Conductivity of MCl/2AlCl₃.

| Structure of M⁺ | Conductivity (mΩcm⁻¹) |
|----------------|------------------------|
| X             | 1.2                    |
| Y              | 1.5                    |
| Z              | 1.3                    |
| W              | 1.7                    |
| V              | 1.8                    |
| U              | 1.9                    |
| T              | 2.1                    |

Table 2 Results of salt spray test.

| Time (hour) | Coating thickness (no chromate) | 5µm | 10µm | 30µm |
|-------------|---------------------------------|-----|------|------|
| 100         |                                 | O   | O    | O    |
| 200         |                                 | O   | O    | O    |
| 300         |                                 | O   | O    | O    |
| 400         |                                 | O   | O    | O    |
| 500         |                                 | O   | O    | O    |
| 600         |                                 | O   | O    | O    |
| 700         |                                 | O   | O    | O    |
| 800         |                                 | O   | O    | O    |
| 900         |                                 | O   | O    | O    |
| 1000        |                                 | O   | O    | O    |
| 1100        |                                 | O   | O    | O    |
| 1200        |                                 | O   | O    | O    |
| 1300        |                                 | O   | O    | O    |
| 1400        |                                 | O   | O    | O    |
| 1500        |                                 | O   | O    | O    |
| 1600        |                                 | O   | O    | O    |
| 1700        |                                 | O   | O    | O    |
| 1800        |                                 | O   | O    | O    |
| 2000        |                                 | O   | O    | O    |
| 2100        |                                 | O   | O    | O    |
| 2200        |                                 | O   | O    | O    |
| 2300        |                                 | O   | O    | O    |
| 2400        |                                 | O   | O    | O    |
| 2500        |                                 | O   | O    | O    |
| 2600        |                                 | O   | O    | O    |
| 2700        |                                 | O   | O    | O    |
| 2800        |                                 | O   | O    | O    |
| 2900        |                                 | O   | O    | O    |
| 3000        |                                 | O   | O    | O    |

<Sample>

<Test condition>

Substrate: Steel
Precasting: Ni 0.3µm
Temperature: 35°C
Spray: 5% NaCl