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# LIMITING CURRENT DENSITY OF ALUMINUM ELECTRODEPOSITION FROM $AlCl_3$-ETHYLMETHYLIMIDAZOLIUM CHLORIDE MELT ON SHEET STEEL

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Synopsis: In order to ascertain a possibility of an industrially continuous Al electroplating to sheet steel, a limiting current density(l.c.d.) of Al deposition from $AlCl_3$-ethylmethylimidazolium chloride melts has been investigated in various electroplating conditions. A maximum l.c.d. was obtained from the melt of 64 mol% $AlCl_3$ in a range of the melt temperature between 60 and 120 °C. Increasing a flow rate and raising the melt temperature had effects of raising the l.c.d..

In the melt of 64 mol% $AlCl_3$ at the flow rate of 2.0 m/s and the temperature of 100 °C, the l.c.d. reached 3.0 $kA/m^2$ or more. The electrodeposited Al obtained under these conditions, had fine crystals without dendritic growth.

Key words: Aluminum electroplating, aluminum chloride-alkylimidazolium chloride melt, limiting current density, Al deposition rate, Al dissolution rate, anodic passivation, melt temperature, $AlCl_3$ concentration, flow rate of the melt.

## 1. Introduction

A pure Al coated steel sheet is expected to be applied to various uses instead of an aluminum sheet. As one of the pure Al coatings, there is an Al electroplating from non-aqueous electrolytes, such as aluminum chloride-alkali chloride melts[1] and organic solutions containing aluminum ions[2]. But, in the Al electroplating from $AlCl_3$-alkali chloride melts, it is a problem that the Al deposit becomes powdery at high current electrolysis ($\geq 15 A/dm^2$), reducing adhesion to a steel substrate[1]. The Al electroplating from organic solutions with aluminum ions also can not be applied to high current electrolysis and these solutions are liable to combustion or ignition[2].

On the other hand, it has been known that an $AlCl_3$-ethylmethylimidazolium chloride (EMIC) melt, which has no danger to ignition and relatively high electroconductivity at low temperature, can be applied as the electrolyte of Al plating[3],[4].

In this study, for the purpose of ascertaining a possibility of an industrially continuous Al electroplating to sheet steel, a limiting current density(l.c.d.) of Al deposition from $AlCl_3$-EMIC melts has been investigated in various electroplating conditions.

## 2. Experimental procedures

A 55 mol% $AlCl_3$-EMIC melt, of which the chemical composition is shown in Table 1, was used as a base electrolyte. And, in a nitrogen-filled glove box, 60-67 mol% $AlCl_3$-EMIC melts were prepared by weighed additions of purified $AlCl_3$ to the base electrolyte.

A beaker cell with stirrer and a high flow rate circulation cell under an atmosphere of purified nitrogen were used to the Al electroplating. Electrodes of both cells were Ni electroplated steel sheet(50 x 50 mm) as a cathode and pure Al plate(99.7%, 50 x 50mm) as an anode. The l.c.d. was defined as a maximum current density that satisfies two

Table 1 Composition of 55 mol% $AlCl_3$-EMIC melt (ppm)

| Al | Mg | Na | Fe | methylimidazolium | cyclohexane | EMI and Cl |
|---|---|---|---|---|---|---|
| 10.7 (mass %) | 2.2 | 1.4 | 3.0 | 3900 | 23 | bal. |

requirements as follows:

(1) A white-colored Al deposit can be obtained.

(2) An electrolytic voltage is not changed during Al electroplating.

Anodic polarization for aluminum plate(99.7%, 1 $cm^2$) and cathodic polarization for Ni electroplated steel sheet(1 $cm^2$) in various compositions of $AlCl_3$-EMIC melts were measured with the beaker cell by the linear potential sweep method(0.05 V/s). The reference electrode compartment which consists of a pure Al wire(99.99%) immersed in 67 mol% $AlCl_3$-EMIC melt, was isolated with a fritted Pyrex disk from the bulk melts.

## 3. Results and discussion

### 3.1 Effects of $AlCl_3$ concentration and melt temperature on limiting current density (l.c.d.)

Figure 1 shows the effects of the $AlCl_3$ concentration and melt temperature on the l.c.d. of Al electrodeposition in the beaker cell with stirrer. The l.c.d. was changed depending on the $AlCl_3$ concentration of melts. And a maximum l.c.d. was obtained from the melt of 64 mol% $AlCl_3$ at all the melt temperature between 60 and 120 °C. The l.c.d. was also increased with raising the melt temperature in all the melts of $AlCl_3$ concentration between 55 and 67 mol%. But, increasing degree of the l.c.d. with the melt temperature was remarkably higher in the melts containing 64 mol% or more than in the melts containing less than 64 mol% $AlCl_3$.

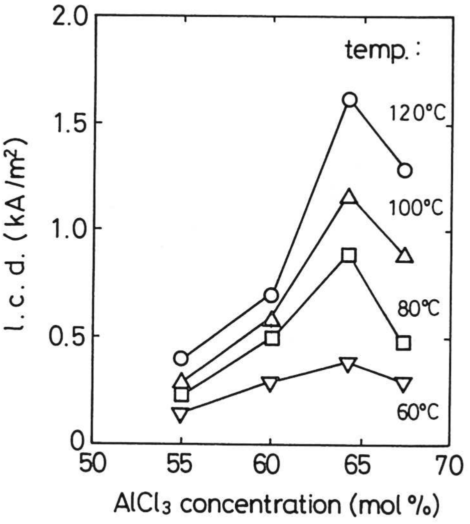


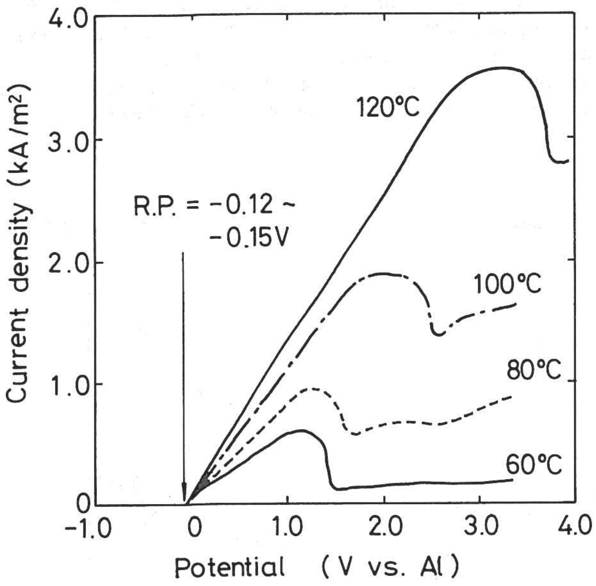
Fig. 1 Effects of $AlCl_3$ concentration and melt temperature on limiting current density(l.c.d.). (beaker cell with stirrer)

Figure 2 shows the anodic and cathodic polarization curves for the 60 mol% $AlCl_3$ melt at various temperatures in the beaker cell with stirrer. In the anodic polarization curve, a peak current density corresponding to the Al dissolution from Al anode was observed at a potential between 1.0 and 3.5 V vs. Al. Also in the cathodic polarization curve, a peak current density corresponding to the Al deposition was at a potential of around -1.2 V vs. Al. In this melt, the anodic peak current density was higher than the cathodic. And the l.c.d. obtained from the 60 mol% $AlCl_3$ melt (Fig.1) agreed with the cathodic peak current density. From Figure 3 showing the anodic and cathodic polarization curves for the 67 mol% $AlCl_3$ melt, the anodic and cathodic peak current densities were also observed at 1.0-1.5 V vs. Al and at around -1.3 V vs. Al, respectively. But, in the 67 mol% $AlCl_3$ melt, the cathodic peak current density was higher than the anodic. The l.c.d. in the 67 mol% $AlCl_3$ melt corresponded to the anodic peak current density. Considering these results, it has been found that in 55-67 mol% $AlCl_3$-EMIC melts, the electrochemical reaction which controls the l.c.d., changes from the Al deposition to Al dissolution with an increase of $AlCl_3$ concentration in the melt. Therefore, the maximum l.c.d. is obtained from the melt of $AlCl_3$ concentration in which the maximum Al dissolution rate (anodic peak current density) becomes equal to the maximum Al deposition rate (cathodic peak current density).

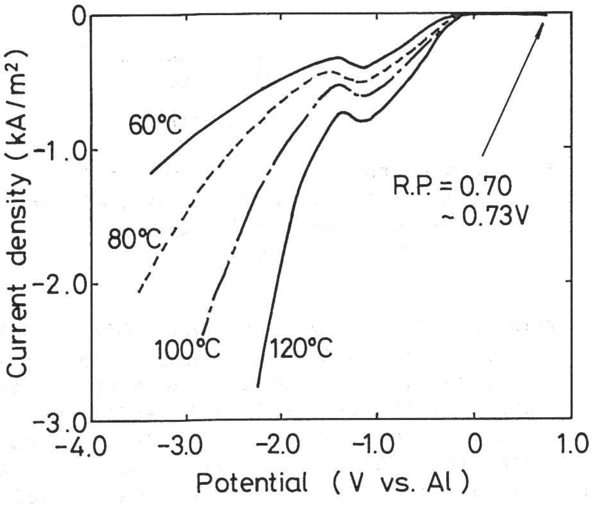
It has been reported that in the $AlCl_3$-EMIC and $AlCl_3$-butylpyridinium chloride melts containing more than 50 mol% $AlCl_3$, anion species mainly consist of $AlCl_4^-$ and $Al_2Cl_7^-$, and a mole ratio of $Al_2Cl_7^-/AlCl_4^-$ becomes higher with $AlCl_3$ concentration of the melts[5],[6]. From the fact that the Al deposition rate and the Al dissolution rate were in inverse relation to increase of $AlCl_3$ concentration of the melt, it is considered that the Al deposition is controlled by a cathodic reaction of $Al_2Cl_7^-$ and that the Al dissolution is controlled by an anodic reaction of $AlCl_4^-$. These Electrochemical reactions are shown as follows.

$$4Al_2Cl_7^- + 3e \rightarrow 7AlCl_4^- + Al \text{ (cathodic reaction)}$$

$$7AlCl_4^- + Al \rightarrow 4Al_2Cl_7^- + 3e \text{ (anodic reaction)}$$

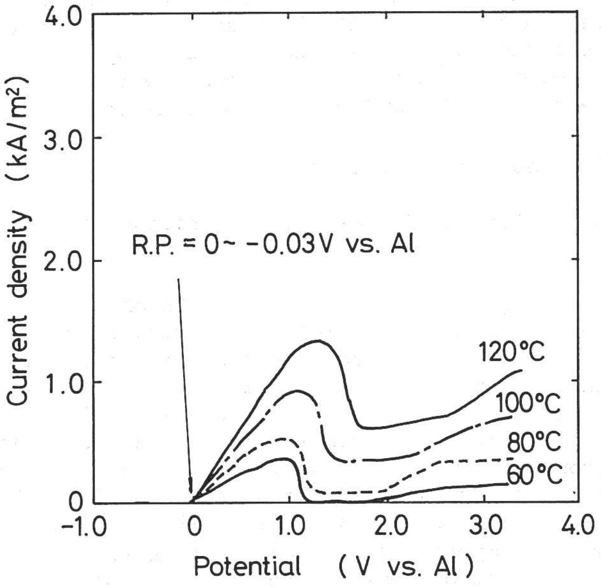


a) Anodic polarization

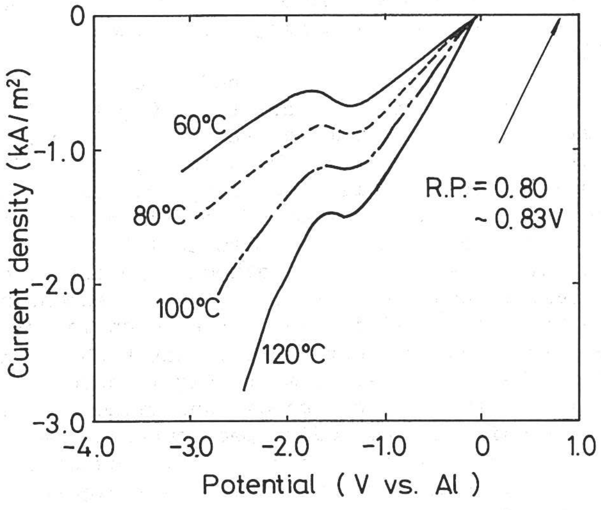


b) Cathodic polarization

Fig. 2 Anodic and cathodic polarization curves for 60 mol% $AlCl_3$-EMIC melt at various temperature.



a) Anodic polarization

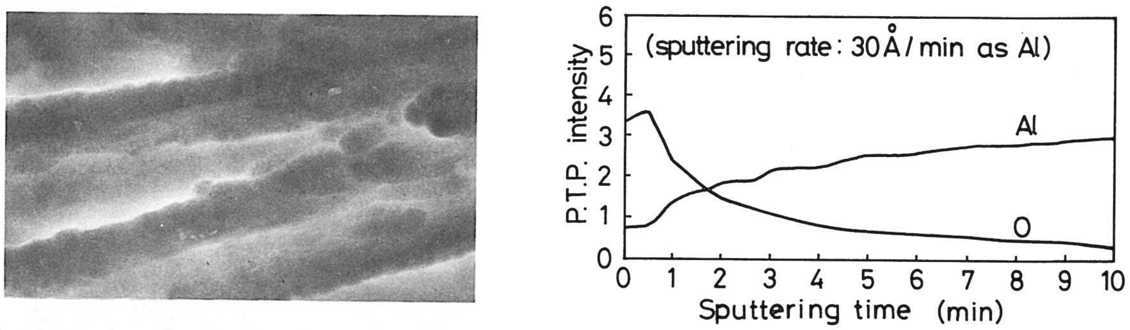


b) Cathodic polarization

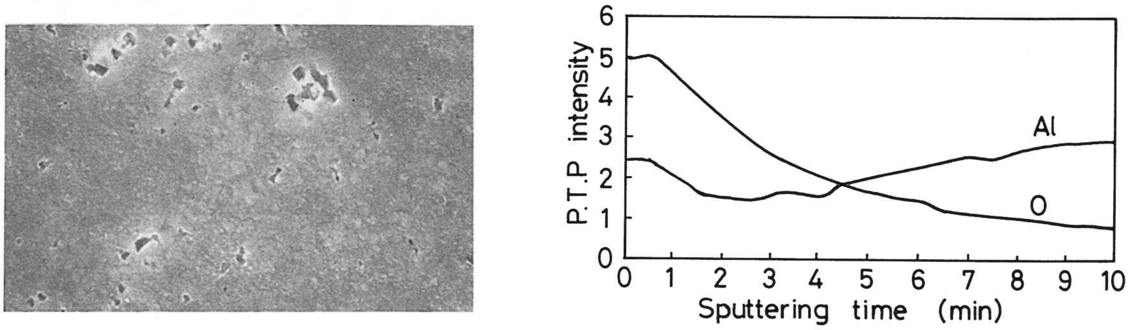
Fig. 3 Anodic and cathodic polarization curves for 67 mol% $AlCl_3$-EMIC melt at various temperature.

(Anode: pure Al plate, Cathode: Ni-electroplated steel sheet
Reference electrode: pure Al wire immersed in 67 mol% $AlCl_3$-EMIC melt)

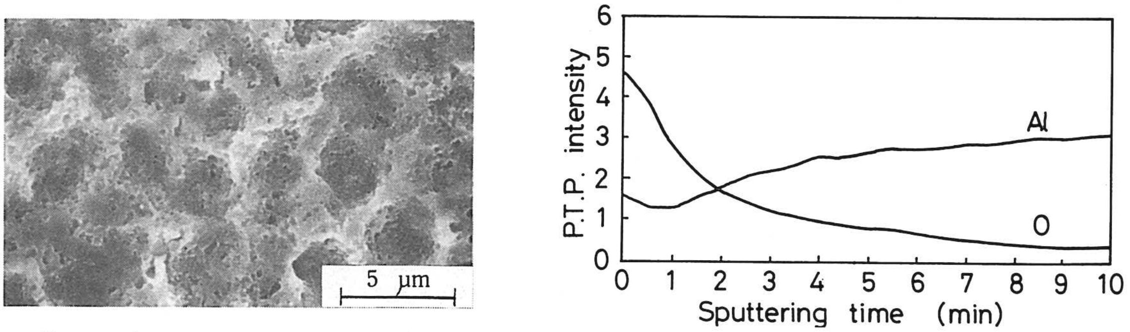
Figure 4 shows the appearance of Al anode and depth profiles of Al and O at the Al anode surface after a potentiostatic electrolysis of 1.9 V vs. Al, higher than the potential corresponded to the anodic peak current density, in the 67 mol% $AlCl_3$ melt at 60 and 120 °C. The Al anode surface electrolyzed at 60 °C of the melt was lustrous and had Al oxide remarkably thicker than that on the Al anode before electrolysis. On the other hand, the Al anode surface obtained from the electrolysis at 120 °C of the melt was dissolved over the whole area and was covered with Al oxide thinner than that formed at 60 °C. From these results, it can be understood that in the melt temperature of 60 °C, the Al dissolution reaction and the Al oxide formation reaction by a slight amount of oxidation species such as $O^{2-}$ and $OH^-$ in the melt occur simultaneously at the near potential corresponding to the anodic peak current density. Under these conditions, an effective and active area of Al anode reduces and an actual current density becomes high. With reducing the active area of Al anode, diffusion rate of $AlCl_4^-$ reaches a maximum, which would make the whole surface of Al anode passive. But, in the melt



a) before electrolysis



b) after electrolysis at melt temperature of 60°C



c) after electrolysis at melt temperature of 120°C

Fig. 4 Appearance of Al anode and AES depth profiles of Al and O at Al anode surface after potentiostatic electrolysis at 1.9 V vs. Al for 60 min in 67 mol% $AlCl_3$ melt at 60 and 120 °C.
*) P.T.P. intensity: peak to peak intensity of each element

temperature of 120 °C, the Al oxide is considered to be very Porous as in the case that formed on the aluminum plate in a hot aqueous solution. Therefore, the fact that the l.c.d. is increased remarkably with temperature of the melt containing 64 mol% or more of $AlCl_3$, would be caused by increasing the diffusion rate of $AlCl_4^-$, controlled the Al dissolution, and forming the porous Al oxide.

### 3.2 Effects of flow rate and melt temperature on limiting current density (l.c.d.) in 64 mol% $AlCl_3$ melt

Figure 5 shows the effects of the flow rate and melt temperature on the l.c.d. in the 64 mol% $AlCl_3$ melt under a high flow rate circulation. Increasing a flow rate of the melt had also an effect of raising the l.c.d.. And, in the 64 mol% $AlCl_3$ melt at the flow rate of 2.0 m/s and the temperature of 100 °C, the l.c.d. reached 3.0 kA/$m^2$ or more. As shown in Figure 6, the electrodeposited Al obtained under these conditions, had fine crystals without dendritic growth. It is understood that the flow rate affected the diffusion rates of $AlCl_4$- controlling the Al dissolution and $Al_2Cl_7^-$ controlling the Al deposition.

From all the results, it is concluded that the continuous Al electroplating is possible industrially, if the 64 mol% $AlCl_3$-EMIC melt of temperature above 100 °C and the electrolytic cell with the flow rate above 1.5 m/s are applied to the Al electroplating.

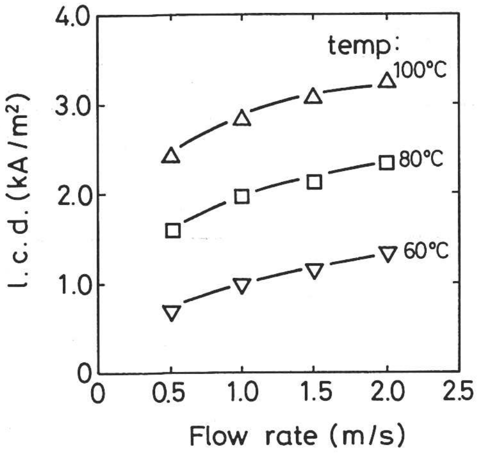


Fig. 5 Effects of flow rate and temperature of melt on limiting current density(l.c.d.) in 64 mol% $AlCl_3$ melt.
(high flow rate circulation cell)

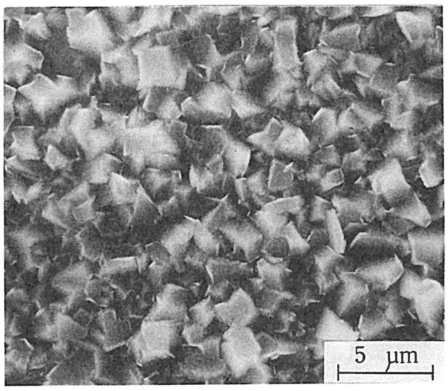


Fig. 6 Surface of Al electrodeposite obtained from 64 mol% $AlCl_3$ melt.
(current density: 3.2 kA/$m^2$
flow rate: 2.0 m/s
melt temperature: 100 °C)

## 4. Conclusion

A limiting current density (l.c.d.) of Al deposition from $AlCl_3$- ethylmethylimidzolium chloride melts has been investigated in various electroplating conditions.

A maximum l.c.d. was obtained from the melt of 64 mol% $AlCl_3$ at all the melt temperature between 60 and 120 °C. In the melts containing less than 64 mol% $AlCl_3$, the Al deposition rate corresponded to the l.c.d. and was not so increased by raising the melt temperature. On the other hand, in the melts containing 64mol% or more of the $AlCl_3$, l.c.d. was determined by the Al dissolution rate from Al anode. The Al dissolution was accelerated remarkably with the melt temperature. Increasing a flow rate of the melt had also an effect of raising the l.c.d..

In the 64 mol% $AlCl_3$ melt at the flow rate of 2.0 m/s and the temperature of 100 °C, the l.c.d. reached 3.0 kA/$m^2$ or more. The electrodeposited Al obtained under these conditions, had fine crystals without dendritic growth.

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