

## Short Communication

## Effect of a high magnetic field on aluminum electrodeposition using an ionic liquid

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## A B S T R A C T

Aluminum electrodeposition on a copper substrate in 1-ethyl-3-methylimidazolium chloride [EMIC]-AlCl<sub>3</sub>, a room temperature ionic liquid, is carried out in a superconducting magnet up to 5 Tesla (T). Linear sweep voltammetry shows an increase in the deposition current, which is explained by the mass transport of reactants enhanced by magnetohydrodynamic (MHD) convection. The application of the magnetic field initiates the formation of nanocrystalline aluminum so that the brightness of the coating is improved. The preferential (2 0 0) orientation is suppressed by increasing the magnetic field intensity, which leads to random orientation in a high magnetic field, corresponding to the formation of fine grains.

## 1. Introduction

Aluminum has a high resistance to corrosion because it can form a dense oxide film on its surface. The smooth surface possesses an excellent ability to reflect visible light and heat [1]. Therefore, Al plating is useful in the production of automobiles, components of optical equipment, mobile devices and electrical appliances. Al thin films can be produced by physical methods, such as sputtering [2] and physical vapor deposition [3], but electrodeposition of Al is also an option [4].

Since Hurlly et al. published their report on AlCl<sub>3</sub>-based ionic liquids for electrodeposition in the 1950s [5], many studies have been carried out on Al electrodeposition [6–14]. In particular, EMIC is commonly used for Al electrodeposition because of its high electrical conductivity, even at room temperature. There have been several reports on the use of additives and pulse plating to form shiny Al coatings. Endres et al. observed that the decomposition of ionic liquids improves the glossiness of a deposited film [15,16]. Stafford et al. reported that the addition of benzene changes the surface morphology and crystal orientation of the Al films [17]. Although many papers have investigated the kinetics and mechanisms of Al electrodeposition, a comprehensive study of the surface morphology and crystallographic structure of Al films electrodeposited using room temperature ionic liquids is still lacking.

Electrodeposition in a magnetic field (*B*) in an aqueous solution has been studied as an attractive method for controlling the surface structure [18–24]. MHD convection is well known to occur during electrodeposition in a magnetic field. When electrodeposition is conducted in a magnetic field, convection in the electrolytic solution is induced by the

electromagnetic interaction,  $J \times B$ , where *J* is the Faraday current density and *B* is the magnetic flux density. The MHD convection changes the mass transport through a new stirring effect [25,26]. When a strong *B* is applied, fine deposits are often obtained under intense MHD convection. In ionic liquids where the solvent is charged, *B* can act directly on the movement of ions, so that more effective results are expected than in aqueous solutions. However, there have been few reports on electrodeposition using ionic liquids in a magnetic field [27].

In this study, Al electrodeposition is performed in a high magnetic field using a superconducting magnet in order to clarify the effects of a magnetic field on the surface morphology and the crystal structure.

## 2. Materials and methods

The experiment was conducted in a closed glass cell filled with argon gas. The electrolyte was an ionic liquid in which EMIC (Merck KGaA, Germany) and AlCl<sub>3</sub> (>98.0%, Kanto Chemical Co., Inc., Japan) were mixed in a molar ratio of 1: 2. A three-electrode system was adopted. A Cu plate (99.9%, Nilaco Corporation, Japan) was used as the working electrode, an Al plate (99.99%, Nippon Light Metal Company, Japan) was used as the counter electrode and an Al wire was used as the reference electrode. The reaction surfaces of the working and counter electrodes were arranged to face each other with a distance of 5 mm between the electrodes. Before the experiments, the Cu substrate was polished using abrasive paper and subsequently etched in a solution containing a mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>. All electrodes were ultrasonically cleaned in acetone and then washed with distilled water. The electrodeposition was conducted with a constant current until the

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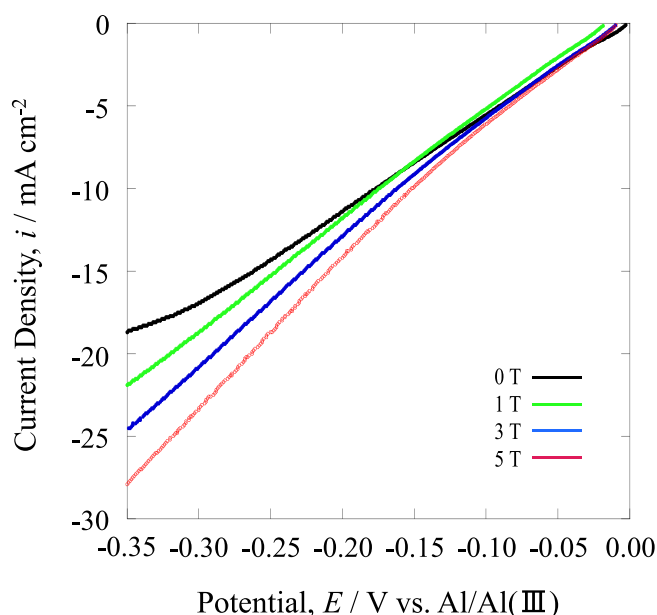
E-mail address: [matsushima@eng.hokudai.ac.jp](mailto:matsushima@eng.hokudai.ac.jp) (H. Matsushima).<https://doi.org/10.1016/j.elecom.2020.106733>

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**Fig. 1.** Linear sweep voltammogram for Cu electrode in an EMIC-AlCl<sub>3</sub> ionic liquid at 60 °C in various magnetic fields: 0 T (black), 1 T (green), 3 T (blue) and 5 T (red) (scan rate: 10 mV/s). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrical charge density reached 29 C cm<sup>-2</sup>. The film thickness corresponded to 10 μm, assuming a current efficiency of 100% for Al electrodeposition. The electrolyte was kept at 60 °C.

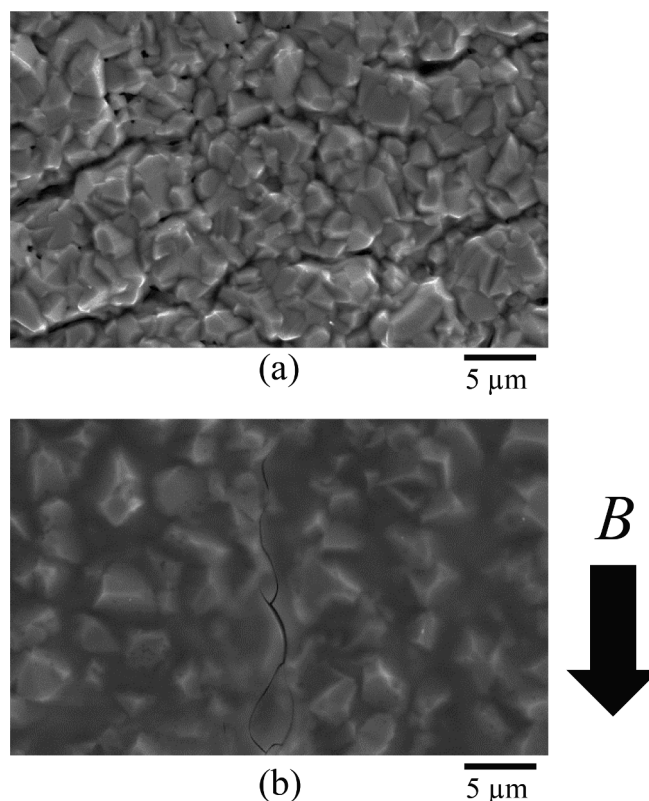
A superconducting magnet (6T-CSM) at the Institute for Materials Research in Tohoku University was used. A uniform magnetic field of up to 5 T was applied parallel to the electrode surface with the field direction from top to bottom. Horizontal MHD convection between the electrodes was therefore observed. The surface morphology was observed by scanning electron microscopy (SEM; JSM-6010PLUS/LA, Jeol, Japan). The crystal structure was studied by X-ray diffraction (XRD; D2PHASER, Bruker, Germany) using the Cu-Kα line.

### 3. Results and discussion

**Fig. 1** shows the results of linear sweep voltammetry. The open circuit potential was around 0 V based on the Al reference, which was independent of the value of  $B$ . In this experiment, the effect of  $B$  on the equilibrium potential was not confirmed clearly [28]. The potential was swept from the open circuit potential to -0.35 V. When the potential was low ( $< -0.15$  V), there was no significant difference in the cathodic current, regardless of  $B$ . Taking into account the results of the equilibrium potential,  $B$  presumably had little effect on the charge transfer reaction.

In the absence of  $B$ , the cathodic current gradually reached a saturated value below approximately -0.3 V. The electrodeposition reaction was dominated by the mass transfer of the reactant ion (Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>). In the presence of  $B$ , the current increased with increasing values of  $B$ . As observed in an aqueous solution, the thickness of the concentration layer became thin owing to MHD convection. The MHD convection promoted the supply of the reactant ion (Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>), which resulted in an increase in the concentration of ions on the electrode surface.

**Fig. 2** shows the surface morphology of the deposit obtained (a) without  $B$  and (b) with  $B = 5$  T. The film obtained without  $B$  was gray and was not shiny. The SEM image shows that the surface has an angular granular texture with a faceted structure (**Fig. 2** (a)). The grain size was approximately 1–5 μm and the size distribution was large. When the magnetic field was applied, the glossiness of the surface improved with increasing values of  $B$ . Some large grains with a facet

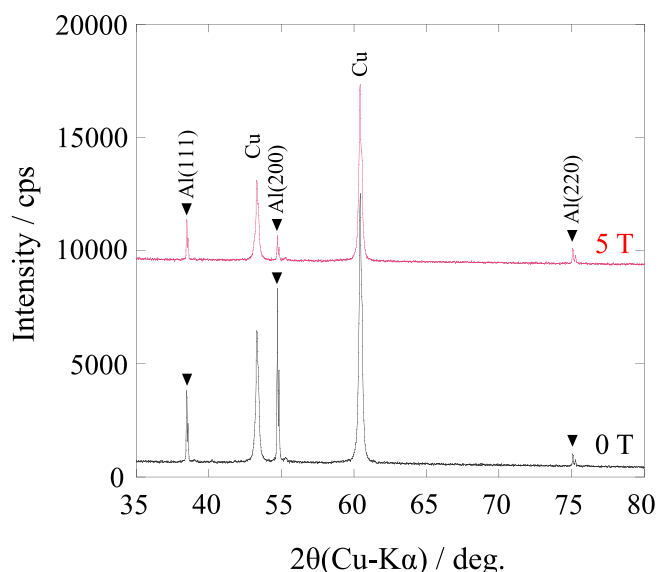


**Fig. 2.** SEM images of Al films electrodeposited in an EMIC-AlCl<sub>3</sub> ionic liquid at 60 °C in magnetic fields of (a) 0 T and (b) 5 T. The arrow shows the magnetic field direction (current density: 20 mA cm<sup>-2</sup>, film thickness: 10 μm).

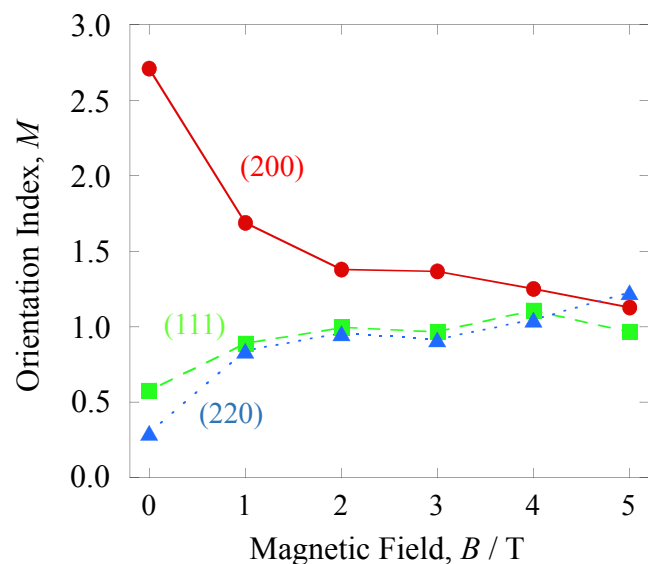
were interpreted on the smooth surface (**Fig. 2** (b)). The surface flatness was attributed to the formation of nanocrystals whose grains could not be observed using the present SEM magnification [15,16].

The deposition process in the absence of a magnetic field is controlled mainly by mass transportation, as suggested by **Fig. 1**. Therefore, a large concentration gradient is formed within a diffusion layer. This causes poor electrical conductivity in the vicinity of the deposits, compared with the aqueous electrolyte. The electric field lines are concentrated on the grain edges, which probably contributes to the preferential nucleation on the facet planes or edges. The newly created deposit mimics the well-orientated structure and grows epitaxially on the facet plane. When a magnetic field is applied, a ready supply of the reactant ion is available between the grain gaps due to MHD convection acting directly on the ionic flow. This is one of the reasons why the gaps between the large grains are filled with fine deposits, resulting in a smooth surface. However, the formation of nanocrystals cannot be explained by the present experiments.

To investigate the crystal structure of the electrodeposited film, XRD measurements were performed. Some strong peaks originating from the Cu substrate and those from the low index planes of Al were observed in the range 35–80° (**Fig. 3**). When a magnetic field was applied, the ratio of the three indexes changed significantly. For a quantitative evaluation, the orientation index (texture number) was calculated (**Fig. 4**) [23]. The (2 0 0) plane was the preferred orientation when Al was electrodeposited in the EMIC system without any additives [8]. This crystallographic feature is related to the faceted morphology, as shown in **Fig. 2**(a). This means that when a new nucleus is formed on a strongly oriented plane, it grows easily by mimicking the substrate crystal structure. The index number of the (2 0 0) plane decreased, but those of (2 2 0) and (1 1 1) increased. As the  $B$  intensity increased, all indexes approached unity, which suggested a random orientation such as a powder diffraction pattern. That is, all the crystal planes existed in



**Fig. 3.** XRD patterns of Al films electrodeposited in an EMIC- $\text{AlCl}_3$  ionic liquid at 60 °C in magnetic fields of 0 T (black) and 5 T (red). Current density: 20  $\text{mA cm}^{-2}$ , film thickness: 10  $\mu\text{m}$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Orientation index,  $M$ , from XRD fundamental reflections of Al films electrodeposited in an EMIC- $\text{AlCl}_3$  ionic liquid at 60 °C under various magnetic field intensities.

the same ratio. It is proposed that there was no difference in the growth rate of the crystal planes when the value of  $B$  is high. Additionally, the non-oriented structure may correspond to the nanocrystal-like deposits (Fig. 2(b)).

In a magnetic field, the concentration of anions on the surface increases owing to enhanced mass transfer by MHD convection [29]. A variation in cation concentration is also produced under electro-neutrality. This may lead to changes in the structure and adsorption of ionic species on the electrode surface [30,31]. Interestingly, some recent papers have reported that the adsorption behavior of ionic liquid is changed by  $B$  [32]. Therefore, because nucleation and film growth occur between the adsorption layer and the surface, the microstructure of the deposits is indirectly affected by  $B$ .

#### 4. Conclusions

We investigated Al electrodeposition from a first-generation ionic liquid  $\text{AlCl}_3$ -EMIC in a superconducting magnet ( $\sim 5$  T). Linear sweep voltammetry measurements revealed the increase in cathodic current depending on the value of  $B$ , and suggested the enhancement of reactant species by MHD convection. The Al deposited at a high value of  $B$  became slightly glossy, which was attributed to the formation of monocrystalline particles among the angular grains with a facet structure. Correspondingly, a random orientation like a powder pattern was formed with  $B$ , while the (2 0 0) plane was the preferential orientation without  $B$ .

Finally, the present results support that the hypothesis that plating in an ionic liquid under a magnetic field has the potential to control the surface structure more than in an aqueous electrolyte, because a charged ionic liquid can be moved by MHD convection or adsorbed irregularly on the surface.

#### CRediT authorship contribution statement

**Hisayoshi Matsushima:** Conceptualization, Methodology, Writing - review & editing. **Hitomi Takahashi:** Investigation, Data curation, Writing - original draft. **Tatsuki Suzuki:** Investigation, Validation. **Mikito Ueda:** Supervision. **Iwao Mogi:** Methodology, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### References

- [1] L. Barchi, U. Bardi, S. Caporali, M. Fantini, A. Scriveri, A. Scriveri, *Prog. Org. Coat.* 67 (2010) 146–151.
- [2] D. Repetto, M.C. Giordano, C. Martella, F.B. de Mongeot, *Appl. Surf. Sci.* 327 (2015) 444–452.
- [3] P.J. Zhang, J.Q. Liu, G.Q. Xu, X.F. Yi, J.W. Chen, Y.C. Wu, *Surf. Coat. Technol.* 282 (2015) 86–93.
- [4] M. Jafarian, M.G. Mahjani, F. Gopal, I. Danaee, *J. Appl. Electrochem.* 36 (2006) 1169–1173.
- [5] F.H. Hurley, T.P. Weir, *J. Electrochem. Soc.* 98 (1951) 207–212.
- [6] T. Tsuda, G.R. Stafford, C.L. Hussey, *J. Electrochem. Soc.* 164 (2017) H5007–H5017.
- [7] M. Ueda, *J. Solid State Electrochem.* 21 (2017) 641–647.
- [8] Q. Wang, Q.Q. Zhang, B. Chen, X.M. Lu, S.J. Zhang, *J. Electrochem. Soc.* 164 (2015) D320–D324.
- [9] A. Bakkar, V. Neubert, *Electrochem. Commun.* 51 (2015) 113–116.
- [10] A. Bakkar, V. Neubert, *Electrochim. Acta* 103 (2013) 211–218.
- [11] J. Tang, K. Azumi, *Electrochim. Acta* 56 (2011) 1130–1137.
- [12] T. Jiang, M.J. Chollier Brym, G. Dube, A. Lasia, G.M. Brisard, *Surf. Coat. Technol.* (2006, 201.) 1–9.
- [13] A.P. Abbott, F. Qiu, H.M.A. Abood, M.R. Ali, K.S. Ryder, *Phys. Chem. Chem. Phys.* 12 (2010) 1862–1872.
- [14] R.T. Carlin, W. Crawford, M. Bersch, *J. Electrochem. Soc.* 139 (1992) 2720–2727.
- [15] S.Z. El Abedin, P. Giridhar, P. Schwab, F. Endres, *Electrochem. Commun.* 12 (2010) 1084–1086.
- [16] Q.X. Liu, S.Z. El Abedin, F. Endres, *J. Electrochem. Soc.* 155 (2008) D357–D362.
- [17] Q. Liao, W.R. Pitner, G. Stewart, C.H. Hussey, G.R. Stafford, *J. Electrochem. Soc.* 144 (1997) 936–943.
- [18] E.A.A. Aboelazm, G.A.M. Ali, H. Algarni, H.J. Yin, Y.L. Zhong, K.F. Chong, *J. Phys. Chem. C* 122 (2018) 12200–12206.
- [19] H.A. Murdoch, D. Yin, E.H. Rivera, A.K. Giri, *Electrochem. Commun.* 97 (2018) 11–15.
- [20] P.W. Zhou, Y.B. Zhong, H. Wang, L.J. Fan, L.C. Dong, F. Li, Q. Long, T.X. Zheng, *Electrochim. Acta* 111 (2013) 126–135.

- [21] J.A. Koza, M. Uhlemann, A. Gebert, L. Schultz, *J. Electroanal. Chem.* 617 (2008) 194–202.
- [22] J.M.D. Coey, G. Hinds, *J. Alloys Compd.* 326 (2001) 238–245.
- [23] H. Matsushima, T. Nohira, I. Mogi, Y. Ito, *Surf. Coat. Technol.* 179 (2004) 245–251.
- [24] O. Devos, A. Olivier, J.P. Chopart, O. Aaboubi, G. Maurin, *J. Electrochem. Soc.* 145 (1998) 401–405.
- [25] L.M.A. Monzon, J.M.D. Coey, *Electrochem. Commun.* 42 (2014) 38–41.
- [26] G. Mutschke, A. Bund, *Electrochem. Commun.* 10 (2008) 597–601.
- [27] H. Takahashi, H. Matsushima, M. Ueda, *J. Electrochem. Soc.* 164 (2017) H5165–H5168.
- [28] F.M.F. Rhen, D. Fernandez, G. Hinds, J.M.D. Coey, *J. Electrochem. Soc.* 153 (2006) J1–J7.
- [29] K. Nishikawa, T. Saito, H. Matsushima, M. Ueda, *J. Electrochem. Soc.* 297 (2019) 1104–1108.
- [30] S. Liu, J. Peng, L. Chen, P. Sebastian, J.M. Feliu, J.W. Yan, B.W. Mao, *Electrochim. Acta* 309 (2016) 11–17.
- [31] R. Atkin, N. Borisenko, M. Druschler, F. Endres, R. Hayes, B. Huber, B. Roling, *J. Mol. Liq.* 192 (2014) 44–54.
- [32] P. Dunne, J.M.D. Coey, *J. Phys. Chem. C* 123 (2019) 24181–24192.