Aluminum barrel plating on steel bolts using chloroaluminate ionic liquids

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Abstract

Al electroplating using ionic liquids (ILs) has been extensively studied for various potential applications, including corrosion-resistant coatings. When Al electroplating is to be performed commercially for many small objects, adopting the barrel plating method is reasonable for improving productivity and reducing manufacturing costs. However, little is known about the barrel-plating conditions for the formation of Al coatings. In this study, the barrel plating conditions for forming Al coatings on steel bolts using ILs composed of 1-ethyl-3-methylimidazolium chloride (EMIC) and aluminum chloride ($AlCl_3$) were investigated. Hull cell tests showed that the IL with an $AlCl_3$/EMIC molar ratio of 1.2 has a higher covering power than the IL with a higher $AlCl_3$ ratio. Barrel plating using the IL with an $AlCl_3$ ratio of 1.2 enabled complete coverage of the bolt with the Al coating. The uniformity of the Al coating on the bolts was further improved by adjusting the rotation speed of the barrel. Furthermore, a simple pretreatment procedure for steel bolts was proposed to obtain an electrodeposited Al coat that adheres well to steel bolts.

Keywords

electrodeposition; electroplating; covering power; ionic liquid

Introduction

Al coatings have many potential applications in various fields, including the aerospace, electronics, and automotive industries, owing to their excellent thermal properties, electrical conductivity, and corrosion resistance.[1] As a technique for fabricating Al coatings, electroplating has advantages over other deposition methods such as chemical and physical vapor depositions, including high deposition rates and the ability to deposit thick layers of up to 1000 μm.[2] Furthermore, in principle, electroplating can offer good coverage even on complex geometries as it is a non-line-of-sight process.[1]

Al cannot be electrodeposited from aqueous solutions; therefore, nonaqueous solutions are required for Al electroplating. Many baths capable of Al electrodeposition have been developed.[1,3,4] Despite their high cost, ionic liquids (ILs) composed of 1-ethyl-3-methylimidazolium chloride (EMIC) and aluminum chloride ($AlCl_3$) are currently the most widely used, owing to their many advantages such as low melting point, low vapor pressure, low flammability, wide electrochemical potential window, and high ionic conductivity. Al electroplating using EMIC–$AlCl_3$ ILs has been extensively studied from various perspectives.[1,3,4] The effects of various deposition parameters, such as the current density,[5] temperature,[6] and composition of the IL,[5,7] on the quality of electrodeposited Al films have been investigated. Additionally, the high resistance of the electrodeposited Al coatings to corrosion was demonstrated.[8,9] However, in most studies, with a few exceptions,[10,11] Al electroplating was performed on a stationary flat plate or a rod-shaped cathode, and little is known about the covering and throwing powers of Al electroplating on objects with complex shapes.[12]

Commercialization of the Al electroplating process requires improving the productivity of the process to reduce manufacturing costs. Unfortunately, Al electrodeposition using ILs must be performed in an inert gas atmosphere (N_2 or Ar) since it is susceptible to moisture and O_2. Therefore, Al electroplating is usually performed in a closed system isolated from ambient air, typically in a glove box. The low workability within the closed system reduces the productivity and increases the cost of electroplating. In particular, when there are many small objects to be electroplated, performing static electrodeposition onto each object individually results in very low productivity and high cost.

One possible way to improve the productivity is to adopt the barrel plating method.[13] Barrel plating is an electroplating method in which objects to be plated are placed in a nonconductive barrel containing an electrolytic bath, and electrodeposition is performed while rotating the barrel to stir the objects and the bath.[14,15] Owing to the large number of small objects being electroplated in one batch, barrel plating can significantly

improve the productivity of Al electroplating. Barrel plating using aqueous baths has long been utilized for electroplating various metal materials such as Cu,[15] Ni,[16] and Zn.[17] However, reports on barrel plating with Al are limited;[11,18] no systematic investigation has been reported on Al barrel plating using ILs and the plating conditions required to obtain a uniform Al coating are unclear.

One potential application of Al barrel plating is in the fabrication of corrosion-resistant Al coatings on steel bolts.[10] The use of Al components in automobiles is on the rise, and when the Al components are fastened with steel bolts, the bolts suffer galvanic corrosion. Coating the surface of the steel bolts with Al protects the bolts from corrosion without altering their mechanical properties.[10]

This study aims to gain insight into the conditions for barrel plating using EMIC–$AlCl_3$ ILs to coat the entire surfaces of steel bolts with Al. The effects of the IL composition and barrel rotation speed on the uniformity of Al coatings electrodeposited on bolts are evaluated. Furthermore, pretreatment of steel bolts to achieve Al coatings that uniformly cover and adhere well to the surfaces of the steel bolts is investigated.

Experimental

All the experiments using EMIC–$AlCl_3$ ILs were conducted in an Ar-filled glove box (UN-800F; UNICO, Japan). The dew point and oxygen content of the Ar atmosphere were maintained below −70 °C and 10 ppm, respectively. All electrochemical experiments were conducted using a potentiostat/galvanostat (PARSTAT4000, Princeton Applied Research).

The EMIC–$AlCl_3$ ILs were prepared by mixing EMIC (Tokyo Chemical Industry, Japan; >97%) that was dried in a vacuum at 120 °C for 48 h and anhydrous $AlCl_3$ (Tokyo Chemical Industry, Japan; > 98%) at the indicated molar ratios. The water content of the dried EMIC was determined to be <30 ppm by Karl Fischer titration; $AlCl_3$ was used as received.

Cyclic voltammetry (CV) was performed in a cylindrical glass cell (VB2-1; EC Frontier, Japan) using a Pt disk electrode with a diameter of 3 mm (PT-6355; EC Frontier, Japan), an Al plate, and an Al wire (99.99%) as the working, counter, and reference electrodes, respectively. The Al wire of the reference electrode was directly immersed in the IL bath. The bath temperature was maintained at 50 °C throughout the measurements, and the scan rate was 10 mV s^{-1}.

Hull cell tests were carried out using a small glass Hull cell (B-55-HG; Yamamoto-MS, Japan), which is a trapezoidal container with a long side of 65 mm, short side of 25 mm, and height of 33 mm. This cell was designed to allow tests to be performed with

one-eighth of the liquid volume (33 mL) of the standard. A Cu plate (34 mm × 50 mm × 0.3 mm, B-60-P05H; Yamamoto-MS, Japan) and an Al plate (32 mm × 32 mm × 0.5 mm, >99%; Nilaco, Japan) were used as the cathode and anode panels, respectively. The IL bath in the Hull cell was heated to 50 °C using a rubber heater wound around the sides of the cell. Electrolysis using the Hull cell was performed at a current of 40 mA for 750 s, without stirring the bath.

Barrel plating was performed using an inclined barrel plater (Yamamoto-MS, Japan). Figure 1 shows a schematic of the barrel plater. An IL bath with a volume of 100 mL and the objects to be plated were placed in a rotating barrel; the rotation axis of the barrel was tilted 60° from the vertical axis. A Ti rod (φ3 mm) covered with perfluoroalkoxy plastic, except for the tip, was used as the cathode. An Al rod (φ3 mm) formed into a vortex with a diameter of approximately 45 mm (Fig. 1) was used as the anode. The anode was set inside the barrel so that the vortex face was approximately 10 mm away from the objects to be plated. A rod-shaped immersion heater (B-82 A; Yamamoto-MS, Japan) and thermocouple were inserted into the bath in the barrel, and the temperature of the bath was maintained at 50 °C during plating. The cathode, anode, heater, and thermocouple inserted into the barrel were fixed to a stationary external support. The objects to be plated were mild steel hex bolts with no surface finishing (HXN-ST-M3-6; SUNCO, Japan), a standard size of M3, pitch of 0.5 mm (JIS B0205:2001(M)), and length of 6 mm. Ni-plated steel bolts with the same dimensions (HXN-STN-M3-6; SUNCO, Japan) were also used as plated objects. Twenty-five bolts were placed in the barrel plater.

Before plating, both the Ni-plated and non-surface-finished bolts were soaked in 5 wt.% NaOH aqueous solution for >24 h and subsequently sonicated in 17 wt.% HCl aqueous solution for 5 min, and rinsed with distilled water and ethanol. Unless otherwise noted, the bolts were dried in a vacuum oven at 60 °C for 48 h and transferred into the Ar-filled glove box before barrel plating.

Barrel plating was performed at a constant current of 105 mA for 9700 s. This applied current corresponds to an average current density of 10 mA cm^{-2} passing through the horizontal projected area of the group of bolts in the barrel. From the dimensions of the bolts (approximately 1.4 cm^2 each) and the quantity of electricity with the assumption of 100% current efficiency, the average thickness of the Al layers formed on the surfaces of all the 25 bolts in the barrel is calculated to be 10 μm. After plating, the bolts were washed with propylene carbonate in the glove box and rinsed with distilled water and ethanol outside the glove box.

After electroplating, the samples were observed using an optical microscope

(BX53; Olympus) and scanning electron microscope (SEM; SU6600; Hitachi High-Technologies). Elemental maps were obtained using an energy-dispersive X-ray spectrometer (INCAxact; Oxford Instruments). A cross-section of the bolt was prepared for observation by embedding the bolt in epoxy resin (EpoxiCure, Buehler), cutting it along the bolt axis, and then mechanically polishing it.

Results and Discussion

$AlCl_3$/EMIC molar ratio

The electroplating conditions were investigated to obtain Al coatings covering the entire surfaces of the bolts via barrel plating. Preliminary experiments revealed that the deposition of Al from the IL was concentrated on the crests of the thread and hardly occurred on the roots. The magnitude of the applied current did not significantly affect the uniformity and coverage of the Al deposits. To achieve full coverage with the Al coating, the effect of the composition of the IL bath, that is, the $AlCl_3$/EMIC molar ratio, was investigated.

Mixing EMIC and $AlCl_3$ generates an IL composed of the EMI^+ cation and $[AlCl_4]^-$ anion, according to Eq. (1).[19] When $AlCl_3$ is added until the $AlCl_3$/EMIC molar ratio exceeds 1, the reaction proceeded as indicated in Eq. (2) to form the $[Al_2Cl_7]^-$ anion. $[Al_2Cl_7]^-$ is electrochemically active and can be reduced to Al metal, whereas $[AlCl_4]^-$ is stable and cannot be reduced. Therefore, Al electrodeposition occurs only when the $AlCl_3$ ratio is greater than 1.[19]

$$\text{EMIC} + AlCl_3 = EMI^+ + [AlCl_4]^- \qquad (1)$$

$$AlCl_3 + [AlCl_4]^- = [Al_2Cl_7]^- \qquad (2)$$

Figure 2 shows the CV profiles of the EMIC–$AlCl_3$ ILs with $AlCl_3$/EMIC ratios of 1.1–1.5. In each CV profile, cathodic and anodic currents due to the electrodeposition of Al and its dissolution are observed. The current for the electrodeposition of Al increased with an increase in the $AlCl_3$ ratio because the concentration of active Al ions, that is, $[Al_2Cl_7]^-$, increases with increasing $AlCl_3$ ratio. In static electroplating, ILs with high $AlCl_3$ ratios (1.5 or higher) are typically used because high electrodeposition rates are generally preferred. However, it is not clear if ILs with high $AlCl_3$ ratios have a high covering power, that is, the ability to produce deposits over a given surface, including recesses.

To gain insight into the covering power of the ILs, Hull cell tests[20] were conducted for the ILs with $AlCl_3$ ratios of 1.2 and 1.5. Figure 3 presents photographs of the cathode panels resulting from electrolysis using the Hull cell at a current of 40 mA for 750 s. Dividing the current by the area of the cathode panel immersed in the electrolyte results

in a calculated average current density of 3.2 mA cm^{-2} for the cathode; however, the local current densities vary depending on the distance from the anode and the nature of the electrolyte. The photographs show that in both ILs, the left side (the side closer to the anode) of the Cu cathode panel was covered with a whitish-gray Al deposit, whereas the right side remained uncovered. The SEM images reveal that the coverage of the Cu panel by the Al deposit decreases with increasing distance from the left edge. A comparison of these panels shows that the IL with an $AlCl_3$ ratio of 1.2 resulted higher coverage over a wider range on the Cu panel than the IL with an $AlCl_3$ ratio of 1.5. At point b with an $AlCl_3$ ratio of 1.2 (18 mm from the left edge), the Al deposit fully covers the Cu cathode, whereas uncovered areas are present with an $AlCl_3$ ratio of 1.5. At point c (28 mm), small uncovered areas start to appear with an $AlCl_3$ ratio of 1.2, whereas the uncovered area expands with an $AlCl_3$ ratio of 1.5. This indicates that the ILs with lower $AlCl_3$ ratios have a higher covering power.

Depending on the $AlCl_3$ ratio, the concentration of the ion species present in the IL varies, and accordingly, the physicochemical properties of the IL vary.[21,22] For example, as the $AlCl_3$ ratio decreases, the concentration of the active Al ion species ($[Al_2Cl_7]^-$) decreases, and the viscosity and conductivity of the IL increase.[21,22] Among these changes, the increase in the conductivity and decrease in the $[Al_2Cl_7]^-$ concentration seem to contribute to the higher covering power. According to a report by Fannin et al.,[21] the conductivity increased from 29 mS cm^{-1} to 34 mS cm^{-1} at 50 °C as the $AlCl_3$ ratio decreased from 1.5 to 1.2. With higher conductivity, the contribution of the IR drop in the electrolyte to the voltage between the anode and cathode is less significant, leading to a more uniform distribution of the local overpotential for Al electrodeposition over the slanted cathode panel. Furthermore, a smaller concentration of active Al ions should result in less dependence of the deposition rate on the overpotential, compared with the case that conforms to the Butler–Volmer equation, because mass transfer of the ions is more likely to affect the deposition rate. For this reason, in ILs with lower $AlCl_3$ ratios, even if an overpotential difference is present, the local deposition rate is somewhat leveled, leading to more uniform Al deposition and higher coverage.

Barrel plating was performed using the two ILs and the Al deposits obtained from each IL were compared. The purpose of the experiment at this stage was to examine the uniformity of the Al deposits on materials with complex shapes; therefore, barrel plating was performed on Ni-plated steel bolts. The Ni layer ensured adhesion of the electrodeposited Al to the bolt. Figure 4 presents optical micrographs of the cross-section of a bolt after barrel plating, showing the electrodeposited Al layer on top of the Ni layer of the bolt. In both ILs, Al was electrodeposited more near the crests than at the roots of

the thread. However, the difference in the thickness of the Al layer at the crest versus the root was smaller when an IL with the low $AlCl_3$ ratio was used. The Al layer formed near the crest was thinner in the bath with the $AlCl_3$ ratio of 1.2 than in that with 1.5 (11.1 μm vs. 19.5 μm), whereas at the root, the Al layer was thicker in the former (4.7 μm vs. 3.5 μm). With the high $AlCl_3$ ratio, there were even areas where no Al was electrodeposited at the roots; however, with the low $AlCl_3$ ratio, Al was electrodeposited on almost the entire surfaces of the bolt, even at the roots. These micrographs clearly show that the IL with the low $AlCl_3$ ratio has a higher covering power in barrel plating, similar to the Hull cell test. In addition, the micrographs show that the Al layer formed from the IL with the low $AlCl_3$ ratio was denser and flatter. The surface SEM images (Fig. 4d and 4h) also show that the Al grains electrodeposited from the IL with the lower $AlCl_3$ ratio are larger and connected, whereas those from the IL with the higher $AlCl_3$ ratio are smaller and isolated at the surface. This difference in microscopic morphology correlates with the covering power of the baths. In the IL with low covering power, because the tendency of preferential electrodeposition at protruding portions of the electrode is more pronounced, the grain growth proceeds more in the vertical direction than in the lateral direction, forming an electrodeposited layer composed of less densely packed grains.

The current efficiency determined from the difference in weight for the bolts before and after the plating was 71% and 61% in ILs with $AlCl_3$ ratios of 1.2 and 1.5, respectively. The lower efficiency in the IL with the higher $AlCl_3$ ratio is probably due to the Al layer being less densely electrodeposited on the bolt surface dropping off more easily when the bolts collide during barrel plating.

The voltage between the cathode and anode during barrel plating was below 2 V, which is within the electrochemical window of the ILs (2.5 V[23]). This indicates that Al dissolution proceeded exclusively at the anode, and the IL did not decompose during plating.

From the results presented above, an IL with an $AlCl_3$ ratio lower than 1.2 may be expected to have greater covering power. However, such an IL limits the electrodeposition rate to a low value because of the very low concentration of active Al ions, increasing the plating time required for the formation of a coat with a certain thickness. To balance the covering power and electrodeposition rate, the IL with an $AlCl_3$ ratio of 1.2 was chosen for the subsequent experiments.

Rotation speed of the barrel

The effect of the rotation speed of the barrel was examined to further increase the uniformity of the electrodeposited Al layer. The barrel plating described above was

performed at a rotational speed of 8 rpm. Figure 5 shows the cross-sections of the bolts after barrel plating, comparing the Al layers formed at rotation speeds of 8, 16, and 24 rpm. Comparing the Al layer obtained at 8 rpm with that obtained at 16 rpm, the latter has a smoother surface and continuously covers the entire surface of the bolt. In addition to the local surface roughness, the difference in the thickness of the Al layer at the root and crest of the thread decreased with an increase in the rotation speed to 16 rpm. However, a further increase in the rotation speed to 24 rpm resulted in the formation of an Al layer with a rougher surface and there were areas where the Al layer was discontinuous, leaving the surface of the bolt exposed. As shown in Fig. 5, the current efficiency (η) for Al electrodeposition was in the range of 59–71% and decreased with increasing rotation speed.

The increase in the surface smoothness and uniformity of the Al layer with an increase in the rotation speed from 8 rpm to 16 rpm is ascribable to the effect of the enhanced agitation of the electrolyte, resulting in a more uniform distribution of the Al active ion concentration on the bolt surface, including the recesses. The decrease in the current efficiency with increasing rotation speed suggests that part of the electrodeposited Al falls off the bolt surface when the bolts collide during barrel plating. The increased roughness at the high rotation speed of 24 rpm was also ascribed to the physical damage caused by the bolts colliding with a higher intensity.

A rotation speed of 16 rpm was optimal for obtaining uniform plating films in the present system. Inspection of the thickness of the Al layer at more than 10 locations on each of the three randomly selected bolts treated under these conditions showed that the thickness was within the range of 2–12 μm.

Direct Al plating on steel bolts

Although barrel plating was performed on Ni-plated steel bolts in the experiments described above, coating Al directly onto steel bolts is more desirable for practical use. However, the adhesion between the steel and electrodeposited Al was not very good without proper pretreatment,[10,11] and therefore, the Al layer exfoliated from the steel bolt during barrel plating.

Metal substrates used for electroplating are typically cleaned with alkaline and acidic aqueous solutions successively to degrease and remove surface oxides. Unlike electrodeposition using aqueous baths, for Al electrodeposition using IL baths, the substrates after pretreatment with aqueous solutions must be thoroughly dried before electrodeposition to avoid introducing residual moisture into the bath. For this purpose, the steel bolts were dried in a vacuum oven at 60 °C for 24 h after aqueous pretreatment

and subsequently transferred quickly into an Ar-filled glove box for Al electroplating. However, a uniform Al layer could not be obtained by barrel plating onto the steel bolts that had undergone this process, as shown in Fig. 6b. Comparison of the appearance of the bolts before and after barrel plating (Fig. 6a and 6b) showed that although whitish-gray Al was partially deposited onto the bolt, Al did not cover the entire surface of the bolt. Oppositely, a uniform Al coating, as shown in Fig. 5, was formed on the Ni-plated bolts treated in the same manner. The formation of oxides on the surface of the steel bolt was suspected to be the cause of the nonuniform Al deposition.

To reduce the chance of oxidation, the procedure was modified as follows: after aqueous treatment, the steel bolts were dried in a vacuum in the transfer chamber of the glove box and then transferred into the glove box without exposure to air. Furthermore, the steel bolts were not heated during vacuum drying, but the drying duration was extended to approximately 48 h. Al barrel plating performed on the bolts treated with this modified procedure yielded a silvery-gray Al coating on the entire surface of the bolt (Fig. 6c).

Figure 7 presents the SEM images and energy-dispersive X-ray spectroscopy (EDX) elemental scanning maps of the cross-sections of the steel bolt shown in Fig. 6c. The maps of the Al and Fe distributions show that an Al layer was formed directly on the surface of the steel bolt. The SEM images show no signs of delamination of the Al layer, indicating that sufficient adhesion between the Al electrodeposit and steel bolts could be obtained by simply drying the bolts at a low temperature without exposing them to air after aqueous treatment. Suppressing reoxidation of the surface of the steel bolt after aqueous treatment was the key to ensuring adhesion. Note that the bolts used in this study were made of mild steel, and more elaborate pretreatment using anodic etching may be necessary for high-strength steel bolts, as reported by Böttch et al.[11]

Immersing the untreated steel bolts in 3% aqueous NaCl solution caused red rust on the surfaces of the bolts within a few days, turning the solution brown and cloudy. In contrast, the bolts coated with the Al layer by barrel plating did not generate red rust even after immersion in the NaCl solution for more than a month, confirming that barrel plating formed an Al coating covering the entire surface of the bolt.

Conclusions

The conditions for Al barrel plating to form Al coatings on steel bolts using EMIC–$AlCl_3$ ILs were examined. The Hull cell tests for ILs with $AlCl_3$ ratios of 1.2 and 1.5 indicated that the IL with the lower $AlCl_3$ ratio had a higher covering power. In barrel

plating onto bolts, an electrodeposited Al layer with a smaller thickness difference between the crests and the roots of the thread of a bolt was obtained when the IL with an $AlCl_3$ ratio of 1.2 was employed. Although Al was deposited discontinuously at the roots from the IL with an $AlCl_3$ ratio of 1.5, a continuous Al layer covering the entire surface of the bolt was obtained from the IL with an $AlCl_3$ ratio of 1.2. Barrel plating results where a higher covering power was obtained at a lower $AlCl_3$ ratio, were consistent with the Hull cell test.

The uniformity of the electrodeposited Al layer was further improved by increasing the barrel rotation speed from 8 to 16 rpm. However, a further increase in the rotation speed to 24 rpm resulted in an Al layer with a rougher surface, probably because the Al layer was physically damaged by the bolts colliding during barrel plating. The current efficiency for Al electrodeposition decreased with increasing rotation speed. The loss of the current efficiency was also ascribed to physical damage.

The issue of the electrodeposited Al not adhering to the steel bolt was resolved by performing barrel plating Al onto the steel bolts that were transferred into the Ar-filled glove box without being exposed to air after pretreatment with aqueous solutions and drying in a vacuum without heating.

These findings can be applied to Al barrel plating on any object and will contribute to the development of Al electroplating technology for industrialization. However, further fine-tuning of the plating parameters may be required, depending on the geometry of the object and its application, especially when plating is performed on a large scale. Future studies on the effects of additives[24] and diluents[25] on barrel plating may help to improve the quality of Al coatings. Various methods for improving the productivity and reducing the cost of Al electroplating have been proposed in the literature, including the development of inexpensive electrolytes[26,27] and methods of Al electrodeposition under ambient atmosphere.[28,29] The feasibility of Al barrel plating combined with these methods should be examined in future studies.

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References

1. K. K. Maniam and S. Paul, *Coatings*, **11**, 80 (2021).
2. M. S. Al Farisi, S. Hertel, M. Wiemer, and T. Otto, *Micromachines*, **9** (2018).
3. C. Li, X. Zhang, and W. He, *J. Mater. Sci. Mater. Electron.*, **29**, 14353–14370 (2018).
4. Y. G. Zhao and T. J. VanderNoot, *Electrochim. Acta*, **42**, 3–13 (1997).
5. T. Jiang, M. J. C. Brym, G. Dube, A. Lasia, and G. M. Brisard, *Surf. Coat. Technol.*, **201**, 1–9 (2006).
6. W. C. Sun, X. Han, and M. Tao, *ECS Electrochem. Lett.*, **4**, D5–D7 (2015).
7. J.-K. Chang, I.-W. Sun, S.-J. Pan, M.-H. Chuang, M.-J. Deng, W.-T. Tsai, *Trans. IMF*, **86**, 227–233 (2008).
8. J.-K. Chang, S.-Y. Chen, C.-H. Tseng, W.-T. Tsai, M.-J. Deng, I.-W. Sun, *Electrochemistry*, **77**, 585–587 (2009).
9. J.-K. Chang, S.-Y. Chen, W.-T. Tsai, M.-J. Deng, I.-W. Sun, *J. Electrochem. Soc.*, **155**, C112 (2008).
10. S. Zein El Abedin and F. Endres, *J. Solid State Electrochem.*, **17**, 1127–1132 (2013).
11. R. Böttcher, A. Valitova, A. Ispas, and A. Bund, *Trans. Inst. Met. Finish.*, **97**, 82–88 (2019).
12. A. P. Abbott, G. Frisch, and K. S. Ryder, *Annu. Rev. Mater. Res. Vol 43*, **43**, 335–358 (2013).
13. R. Singleton, *Met. Finish.*, **97**, 346–367 (1999).
14. Y. Hoshino, *J. Surf. Finish. Soc. Japan*, **68**, 586–593 (2017).
15. K. H. Han, S. B. Lee, and I. K. Hong, *J. Ind. Eng. Chem.*, **18**, 888–897 (2012).
16. I. K. Hong, H. Kim, and S. B. Lee, *J. Ind. Eng. Chem.*, **20**, 3767–3774 (2014).
17. J. Y. Hihn, M. Wery, and J. C. Catonne, 165–172 (2000).
18. E. L. Smith, C. Fullarton, R. C. Harris, S. Saleem, A. P. Abbott, K. S. Ryder., *Trans. IMF*, **88**, 285–293 (2010).
19. T. Tsuda, G. R. Stafford, and C. L. Hussey, *J. Electrochem. Soc.*, **164**, H5007–H5017 (2017).
20. M. Miyake, Y. Kubo, and T. Hirato, *Electrochim. Acta*, **120**, 423–428 (2014).
21. A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, *J. Phys. Chem.*, **88**, 2614–2621 (1984).
22. V. A. Elterman, P. Y. Shevelin, L. A. Yolshina, E. G. Vovkotrub, and A. V. Borozdin, *J. Mol. Liq.*, **320**, 114482 (2020)

23. H. Ohno, *Electrochemical Aspects of Ionic Liquids*, p. 1–392, John Wiley and Sons, (2005).
24. Q. Zhang, Q. Wang, S. Zhang, and X. Lu, *J. Solid State Electrochem.*, **18**, 257–267 (2014).
25. A. P. Abbott, F. Qiu, H. M. A. Abood, M. R. Ali, and K. S. Ryder, *Phys. Chem. Chem. Phys.*, **12**, 1862–1872 (2010).
26. T. Jiang, M. J. C. Brym, G. Dube, A. Lasia, and G. M. Brisard, *Surf. Coat. Technol.*, **201**, 6309–6317 (2007).
27. H. M. A. Abood, A. P. Abbott, A. D. Ballantyne, and K. S. Ryder, *Chem. Commun.*, **47**, 3523–3525 (2011).
28. A. P. Abbott, R. C. Harris, Y-T. Hsieh, K. S. Ryder, I-W. Sun, *Phys. Chem. Chem. Phys.*, **16**, 14675–14681 (2014).
29. M. Yamagami, S. Higashino, T. Yamamoto, T. Ikenoue, M. Miyake, T. Hirato, *J. Electrochem. Soc.*, **169**, 062502 (2022).

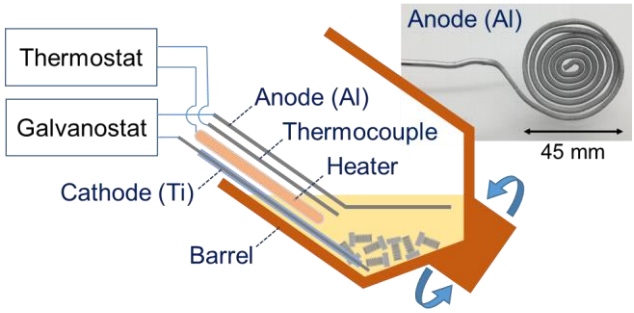

Fig. 1: Schematic of barrel plater employed in this study.

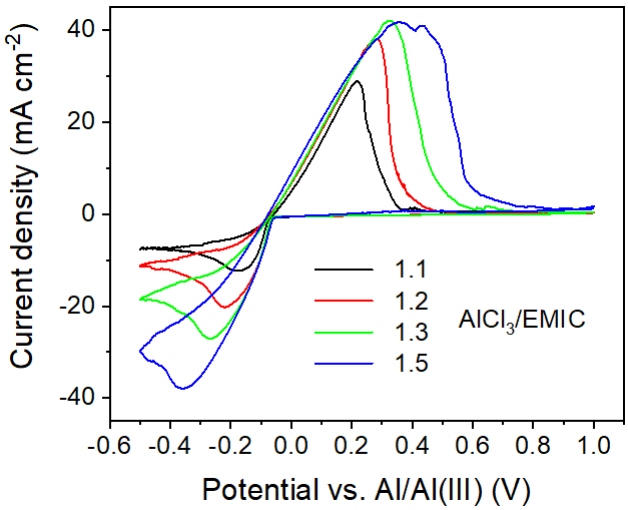

Fig. 2: CV profiles for EMIC–$AlCl_3$ ILs with $AlCl_3$/ EMIC molar ratios of 1.1–1.5.

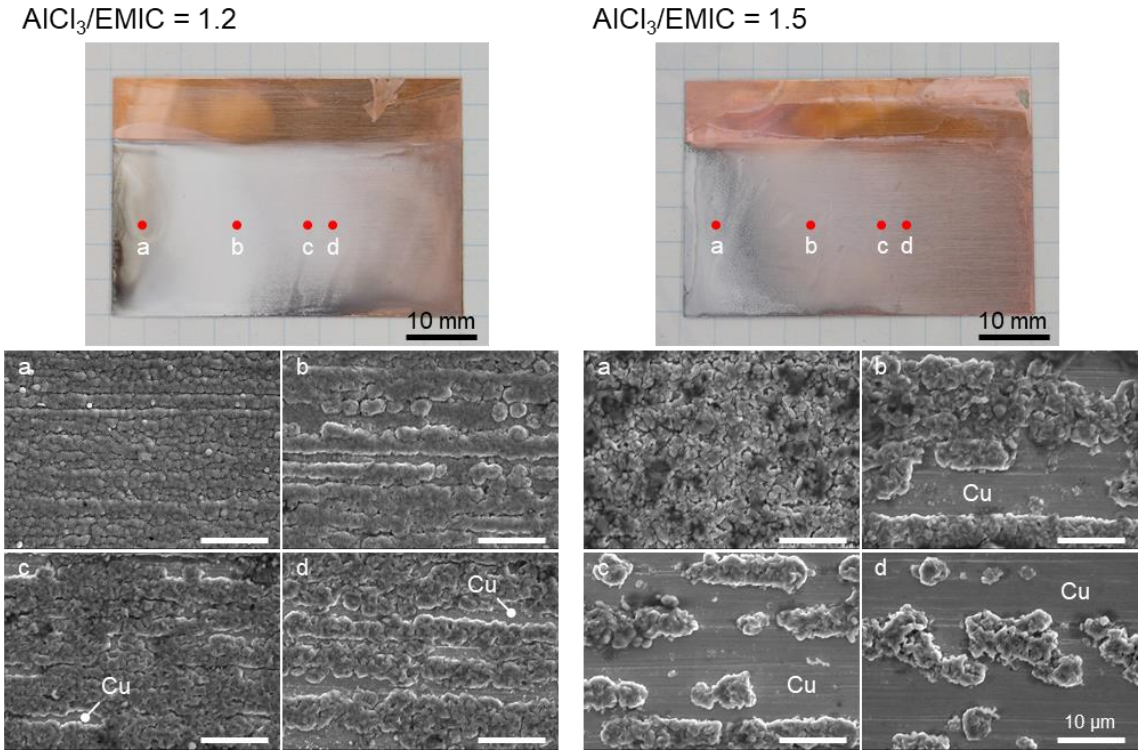

Fig. 3: Photographs of Cu cathode panels after Hull cell test for EMIC–$AlCl_3$ ILs with $AlCl_3$/EMIC molar ratios of 1.2 and 1.5; SEM images of the cathode surface at the points indicated in the photographs. Points a, b, c, and d are located at 5, 18, 28, and 32 mm, respectively, from the left edge of the cathode panel.

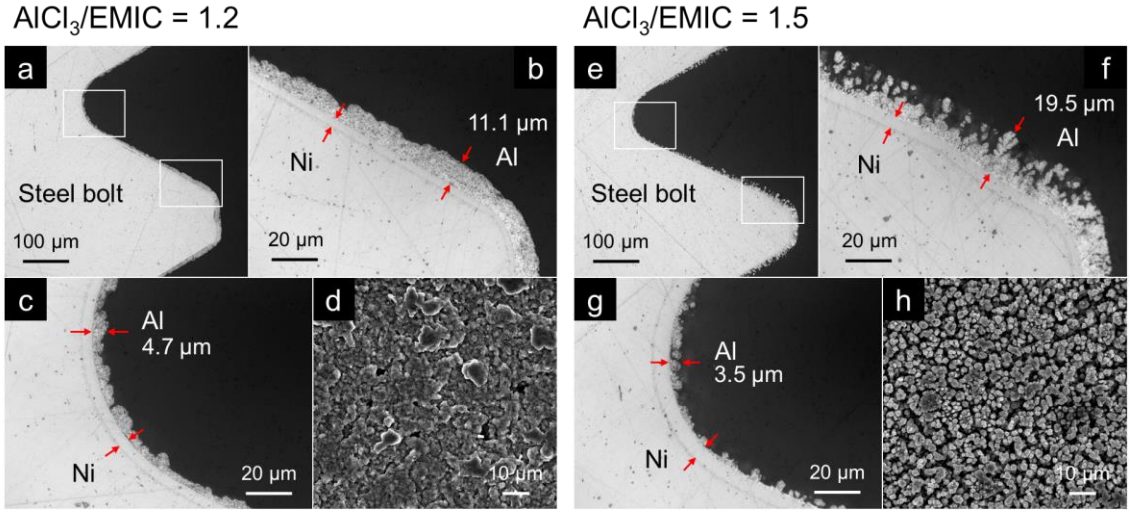

Fig. 4: (a–c, e–g) Optical micrographs of cross-sections of Ni-plated steel bolts after Al barrel plating using the ILs with $AlCl_3$ ratios of 1.2 and 1.5. (d, h) SEM images of the surface of the Al layer deposited on the bolts. The barrel rotation speed was 8 rpm.

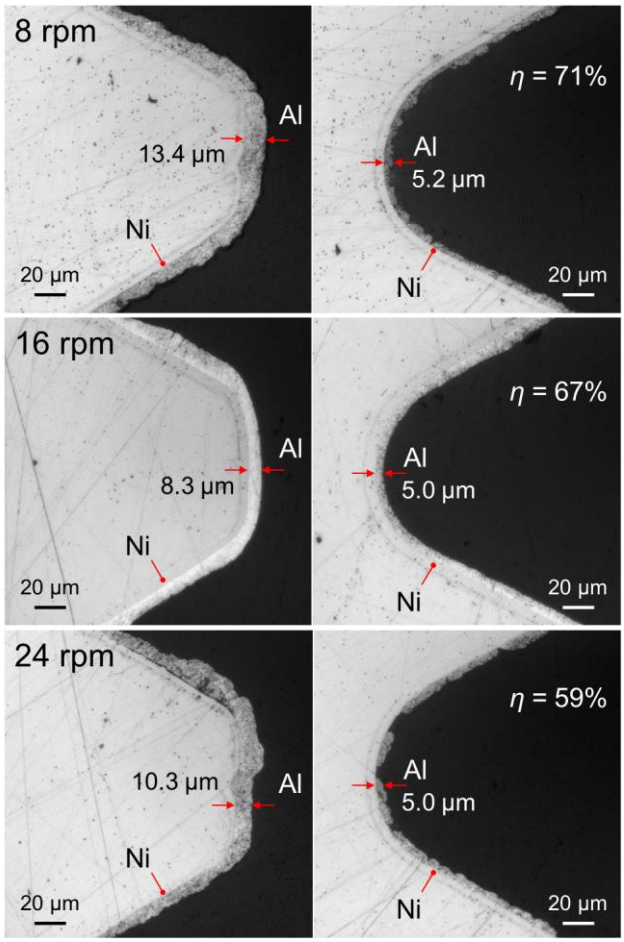

Fig. 5: Optical micrographs of cross-sections of Ni-plated steel bolts after Al barrel plating using the IL with $AlCl_3$ ratio of 1.2 at barrel rotation speeds of 8, 16, and 24 rpm. The current efficiency (η) for Al electrodeposition under the aforementioned conditions is indicated in the figures.

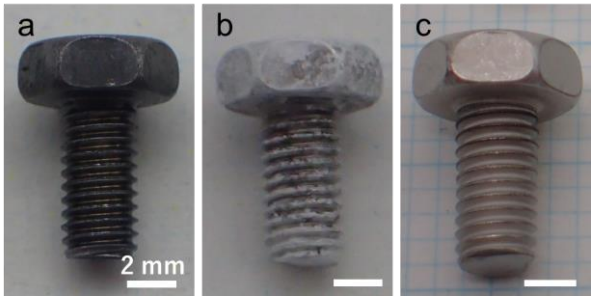

Fig. 6: Photographs of (a) as-received steel bolt and (b, c) bolts after Al barrel plating. Before Al plating, the bolts were pretreated with aqueous solutions, and subsequently underwent the following processes: (b) dried under reduced pressure at 60 °C in a vacuum oven, quickly transferred into the Ar-filled glove box through ambient air, and (c) dried under reduced pressure without heating in the transfer chamber of the glove box, and transferred into the glove box without being exposed to the air.

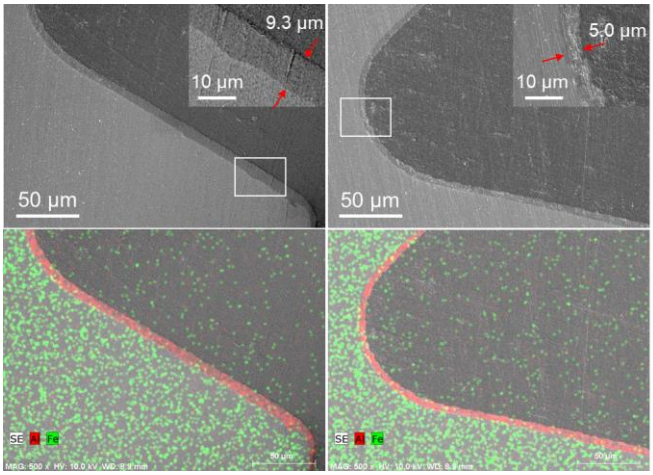

Fig. 7: SEM images and EDX elemental scanning maps for Al (red) and Fe (green) in cross-sections of a steel bolt after Al barrel plating.