Paper

Clarification of the Anodic Dissolution Behavior of Metallurgical Structures during Electrorefining of Al-Mn Alloys in a 1-Ethyl-3-Methyl-Imidazolium Chloride-AlCl₃ Ionic Liquid*

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Recycling Al is crucial to reduce the energy and environmental costs of Al manufacturing; however, the reclamation efficiency of high-quality Al from Al alloys is limited by the co-deposition of impurities during the electrorefining process. To address this issue, the anodic dissolution behavior of metallurgical structures within various Al-Mn binary alloys in 1-ethyl-3-methyl-imidazolium chloride-AlCl₃ ionic liquid was investigated. During the constant-potential electrolysis of Al-1.5%Mn casting and cold-rolled plate alloys, an enriched layer derived from Mn solid solution was formed at an electrorefining potential of 0.2 V; this was attributed to preferential dissolution of Al in the matrix phase, followed by Mn accumulation at the Al surface. Furthermore, dissolution of the Al-Mn-Fe and Al-Mn intermetallic compounds occurred at 0.6 and 1.0 V, respectively; thus, the dissolution behavior of Mn in the Al-Mn alloys differed between the Mn solid solution in the matrix phase and the Mn containing intermetallic compounds. These results indicate that by controlling the microstructure of the Al-Mn alloy and the applied anodic potential, the dissolution of Mn into the 1-ethyl-3-methyl-imidazolium chloride-AlCl₃ electrolyte can be suppressed, thus preventing its co-deposition with Al on the cathode. This development is therefore anticipated to inform the development of electrorefining processes to obtain high-quality recycled Al for numerous manufacturing applications.

Keywords: anodic dissolution, electrorefining, Al-Mn alloy, metallurgical structure, ionic liquid

1. Introduction

Manganese is one of the main additives used to manufacture aluminum alloys. Al-Mn alloys have the same level of workability as pure Al with the additional advantages of improved corrosion resistance and superior mechanical properties. Thus, Al-Mn alloys are used in many manufacturing applications, including the production of beverage cans, automotive parts, and construction materials^{1)~4}. When recycling products comprising these alloys, the Al has a lower melting point than metals such as Fe, and consequently, scrap Al is easily remelted and recycled; the reclaimed raw Al materials are called recycled Al. Recycled Al has a low environmental impact because it can be produced with 3-5% of the energy consumption of primary Al produced via the Hall-Heroult process^{5)~7)}, which requires 13,000-15,000 kWh t⁻¹-Al of electrical energy and produces CO_2 emissions during the electrolysis stage^{7)~9)}. Further promotion of the use of recycled Al is desirable for realizing a sustainable society. However, manufacturing high-quality wrought materials from Al sources other than primary Al is difficult; in particular, Al recycled from automobile scrap contains various elements as impurities, thus reducing the physical quality of the manufactured alloys. Recycled Al derived from automobiles is primarily used as raw materials for casting and diecasting alloys that can be manufactured with lower

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quality benchmarks^{10), 11)}. This type of recycling, which produces materials of progressively decreasing quality, is called cascade recycling, which eventually results in Al scrap that is difficult to reprocess^{11), 12)}. However, if further recycling of this lower-quality Al scrap can be achieved, this could lead to more efficient use of resources and a further reduction in environmental impact. Previously, we proposed a recycling process using electrorefining to solve this problem^{13), 14)}. Recycling via the electrorefining method has been previously attempted using molten salts ^{5), 15)} or ionic liquids as $electrolytes^{16)\sim 20}$. These reports found that the concentrations of various additive elements in Al scraps were reduced by electrorefining, thus increasing the quality of the final Al product.

Our previous studies particularly focused on methods that use ionic liquids as electrolytes. This method can save energy during electrorefining because the energy required to maintain the bath temperature is low compared to the Hall-Heroult process. Among the ionic liquids capable of Al electrodeposition, 1-ethyl-3-methyl-imidazolium chloride-AlCl₃ ionic liquid with the highest conductivity was selected²¹⁾. In this method, solid Al alloys are used as anodes in low-temperature electrolytes. Because solid solutions and complex intermetallic compounds are formed in Al alloys depending on the additive elements and manufacturing methods involved, it is important to understand the anodic dissolution behavior of Al alloys concerning their metallurgical structures in detail. Previously, we reported the anodic dissolution behavior and electrorefining behavior of Al-Si alloys¹³⁾ and Al-Cu alloys¹⁴⁾ as anodes. In the former case, we found that Al preferentially dissolves from the anode surface because of the decreased solubility of Si in the electrolyte; high-purity Al can therefore be recovered at the cathode. However, the Al₂Cu intermetallic compound in the Al-Cu alloy dissolves into the electrolyte depending on the applied potential. Thus, precise control of the anodic potential during electrorefining is important for recovering high-purity aluminum at the cathode. Understanding the anodic dissolution behavior of individual metallurgical structures is, therefore, necessary to enable the design of suitable anodes for electrorefining; however, studies examining this have yet to be carried out thus far. As mentioned previously, Mn is a major additive element for Al alloys and forms solid solutions or intermetallic compounds in the alloy matrix²²⁾. However, Mn forms more complex metallurgical structures than Si and Cu, such as Al-Mn-Fe and Al-Mn-Fe-Si^{3, 23)~25)} including impurities of Fe or Si derived from primary aluminum. In addition, Al-Mn binary intermetallic compounds, such as Al₆Mn and Al₁₂Mn, can be formed. Furthermore, when Mn ions are present in the electrolyte, Mn and Al are easily co-deposited onto the cathode^{26)~29}. To remove Mn from Al scrap, it is, therefore, necessary to prevent the dissolution of Mn from the anodes. The electrolysis conditions under which Mn is retained in the anode must be clarified, in addition to the metallurgical structures which inhibit anodic dissolution of Mn. In this study, the anodic dissolution and cathodic deposition behaviors of various Al-Mn binary alloys with controlled Mn compositions and intermetallic compound types and sizes were investigated. Particular focus was maintained on the metallurgical structures of the alloys, which were investigated with several physical analysis techniques. By examining these two aspects, it was anticipated that the optimal electrorefining conditions, anode composition, and anode structure would be found to enable high Al recycling efficiencies from Al-Mn alloys.

2. Experimental

A 99.5%Mn rod (ϕ =6.35 × 50 mm, Goodfellow, U.K.), 99.999%Al (0.5 mm thickness, Nilaco, Japan), and Al-xMn (x=0.5, 1.0, and 1.5%Mn) casting alloys and cold-rolled plates were used as the anode specimens. Casting alloys with 175 × 175 × 34 mm dimensions were produced using a semi-continuous (direct chill casting) method with 99.9% primary Al and an Al-Mn (12%Mn) matrix alloy. Subsequently, the samples were cut to a thickness of 30 mm and ground flat on either side. Cold-rolled sheets were fabricated by heat treatment and subsequent rolling of the treated alloys. First, the casting alloys were homogenized in an electric furnace at 823 K for 6 h, followed by hot

rolling to a thickness of 3 mm. After intermediate annealing at 623 K for 1 h, the alloy sheets were cold rolled to a thickness of 1 mm. The compositions of the casting and cold-rolled alloys were then determined using an optical emission spectrometer (ARL4460, Thermo Fisher Scientific, U.S.A). At the same time, their electrical conductivities were measured using a conductivity meter (SIGMATEST 2.069, FOERSTER, U.S.A.). The preparation of the ionic liquid electrolyte and the electrochemical measurements were performed in a glove box under an Ar atmosphere. The electrolyte was prepared by mixing 1-ethyl-3methyl imidazolium chloride (EmImCl, 96%, Tokyo Chemical Co., Ltd., Japan) and AlCl₃ (97%, Kanto Chemical Co., Ltd., Japan) at a respective molar ratio of 1:2. To remove water and impurities into the electrolyte, the Al wire was immersed in the ionic liquid electrolyte for over 48 h at 323 K before the electrochemical measurements. Before the Al wire was immersed, the ionic liquid was yellow and opaque. After immersion of Al wire, the ionic liquid became clear from which water and impurities had been sufficiently removed. Electrochemical measurements were conducted in a three-electrode cell using a Mn rod, high-purity Al, or various Al-Mn alloys as the working electrode, a Pt or Cu plate as the between the working and counter electrodes was fixed at 20 mm. The electrolyte was heated to 323 K using a hot-plate stirrer. Each electrode was connected to a potentiostat (HZ-Pro, Hokuto Denko Co., Ltd., Japan) for the linear sweep voltammetry and constant-potential electrolysis. After 20 min of specimen immersion in the electrolyte, voltammograms were obtained between the immersion potential and 1500 mV at scanning rates of 0.3, 0.5, 1, 5, and 10 mV s⁻¹. Constant-potential electrolysis was performed at potentials of 0.2, 0.4, 0.6, and 1.0 V and electric charge densities of 1, 3, 5, 10, 20, 30, and 100 C cm⁻². After the constant-potential electrolysis experiments, the anode specimens were rinsed with distilled water and dried. Visual observations, X-ray diffraction (XRD, D2PHASER, Bruker, U.S.A), scanning electron microscopy (SEM, JSM-6610, JEOL, Japan), and field-emission scanning electron microscopy (FE-SEM, JSM-7200F, JEOL, Japan) were then carried out on the anode specimens.

Additionally, the cathode specimens were rinsed with distilled water and dried, followed by visual and SEM observations. The electrodeposits on the cathodes were collected and examined using SEM. The composition of the anode and electrodeposits on the cathode were analyzed by energy dispersive spectroscopy (EDS) equipped with FE-SEM. The specimens obtained before and after the constantpotential electrolysis were embedded into cold polyester resin, cut, polished with 220-2400 grit waterresistant polishing paper, and finished to a mirror-like surface using 9, 3, and 1 µm diamond sprays (DP-Spray, Struers, Denmark). Their cross-sections were then examined via field-emission electron probe micro-analysis (FE-EPMA JXA-8530F, JEOL, Japan), FE-SEM, and EDS. EPMA is used wavelength dispersive spectroscopy (WDS) as a detector; WDS has higher detection sensitivity and energy resolution than EDS, and is effective for detecting trace elements. EPMA was used to confirm the distribution state of trace elements in the manufactured Al-Mn alloys before electrolysis experiments.

3. Results

3.1. Evaluation of Al-Mn alloy specimens

The compositions of various Al-Mn alloys obtained by optical emission spectroscopy (OES) are listed in **Table 1**. The obtained Al-Mn alloys contained impurities such as Si, Fe, and Cu, derived from the primary Al source in the fabrication process. The variation in the electrical conductivity of the Al-Mn alloys, concerning the amount of Mn added, and the results of the cross-sectional EPMA analysis of the Al-1.5%Mn alloy are shown in **Fig. 1**. The theoretical electrical conductivity (σ) for Al-Mn solid solution alloys of international annealed copper standard (IACS) quality³⁰ was calculated from Eq. (1)^{31), 32}, in which Matthiessen's rule was applied to the case of binary alloys via the conversion formula in Eq. (2):

$$\rho_{\rm SS}(T) = \rho_{\rm pure} + C_{\rm Mn} \,\Delta \,\rho_{\rm Mn}(T) \tag{1}$$

$$\sigma = (\rho_{\rm Cu}(T) / \rho_{\rm SS}(T)) \times 100 \tag{2}$$

where ρ_{SS} is the resistivity of the solid solution



 Table 1
 The elemental composition of the Al-Mn alloy specimens produced for this study.

Fig. 1 (a) The theoretic and measured electrical conductivities of various Al-Mn binary alloy specimens;(b) Cross-sectional SEM images and corresponding FE-EPMA profiles of Al, Mn, and Fe of the Al-1.5%Mn casting alloy and cold-rolled plate specimens. alloys, and the solid lines represent the cold-rolled plates.

alloy (Al-Mn) at temperature T, ρ_{pure} is the resistivity of the pure metal (Al) at T^{33} , C_{Mn} is the concentration of the Mn solid solution in the Al matrix, $\Delta \rho_{\text{Mn}}$ is the contribution of Mn to the resistivity per unit of concentration at T^{33} , and $\rho_{\text{Cu}}(T)$ is the resistivity of pure copper at T^{30} . Each constant was calculated using values obtained at room temperature.

The electrical conductivity measurements (Fig. 1(a)) show that the electrical conductivities of the casting alloys are close to their theoretical values, whereas those of the cold-rolled plates are higher. This can be attributed to the increased amount of Mn in the latter specimen type. The results of the cross-sectional EPMA analysis (Fig. 1(b)) of the Al-1.5%Mn casting alloy show that Al-Mn-Fe intermetallic compounds exist in the Al matrix as particles approximately 10 µm in diameter. In the cold-rolled plate, these particles have grain sizes of several micrometers. Additionally, particles consisting of only Al and Mn were detected, thus indicating that Al-Mn-Fe and Al-Mn intermetallic compounds were present simultaneously in the Al matrix phase.

3.2. Electrochemical measurement

3.2.1. Linear sweep voltammetry

Linear sweep voltammogram for 99.5% Mn, 99.999% Al, and the various Al-Mn alloys are shown in **Fig. 2**. The voltammograms (Fig. 2(a)) show that the

current density of 99.5% Mn increases linearly with the immersion potential (versus Al/Al(III)); however, for 99.999%Al, the current density only increases linearly to approximately 0.4 V before sharply decreasing as the potential reaches 0.5 V. The current density then increases further until a steady-state plateau is reached at approximately 0.9 V. A similar trend was observed for the Al-Mn alloys, where steady-state current densities were obtained at potentials above 0.8, 0.9, and 1.0 V for the Al-0.5%Mn, Al-1.0%Mn, and Al-1.5%Mn casting alloys and coldrolled plates, respectively. These results indicate that the maximum current density increases with the amount of Mn incorporated into the alloy; however, no significant difference in linear sweep voltammetry behavior was observed between the casting alloy and the cold-rolled plate for each Al-Mn composition. The maximum current densities for 99.999% Al fell between Al-1.0%Mn and Al-1.5%Mn.

Voltammograms obtained for the Al-1.5%Mn casting alloy and cold-rolled plate at scanning rates of 0.3-10 mV s⁻¹ are shown in Figs. 2 (b)-(e). From Fig. 2(a), the dissolution potential of Mn was determined to be 0.11 V compared to the Al reference electrode. In the voltammograms obtained for the Al-1.5%Mn casting alloy (Fig. 2(b)), the potential associated with the maximum current density increases with the scanning rate, accompanied by an increase in the





Fig. 2 Voltammograms obtained using linear sweep voltammetry for: (a) 99.999%Al, 99.5%Mn, and various Al-Mn alloys; (b), (c) the Al-1.5%Mn casting alloy at various scanning rates; (d), (e) the Al-1.5%Mn cold-rolled plate alloy at various scanning rates. All measurements were conducted in a 1 : 2 EmImCl-AlCl₃ ionic liquid at a temperature of 323 K.

maximum current density itself. At scanning rates of 5 and 10 mV s^{-1} , the current density reaches a minimum and remains at that value with increasing potential, whereas the curves obtained at scanning

rates of 0.3, 0.5, and 1 mV s^{-1} exhibit steady-state plateaus at approximately 2 mA cm^{-2} . At the beginning of the measurements (Fig. 2(c)), an inflection point was observed in each voltammogram at about 50 mV, which increased in magnitude as the scanning rate decreased. This value is lower than the observed dissolution potential of Mn (0.11 V) in the ionic liquid electrolyte. Similar trends were observed for the Al-1.5%Mn cold-rolled plates (Fig. 2(d) and (e)).

3.2.2. Constant potential electrolysis

The obtained FE-SEM images of the surfaces of Al-1.5%Mn casting alloys and cold-rolled plate anodes after constant-potential electrolysis at potentials between 0.2-1.0 V (electric charge density = 30 C cm^{-2}) are shown in Fig. 3. The surface roughness of the casting alloys and the cold-rolled plates decreased as the potential became more noble. The SEM images of the casting alloy specimens (Fig. 3(a)) were obtained under high magnification (as marked by the insets in each FE-SEM image), and the linear features on each surface were analyzed by energy dispersive spectrometry (EDS). As in the EPMA results (Fig. 1(b)), In casting alloy, particles containing Al, Mn, and Fe were detected, thus indicating the presence Al-Mn-Fe intermetallic compounds in the alloys. These Al-Mn-Fe intermetallic compounds were (91.6-92.2)at%Al-(4.7-5.0)at%Mn-(3.2-3.4)at%Fe, regardless of potential. Dissolution at the surfaces of the Al-Mn-Fe intermetallic compounds was also observed at potentials above 0.6 V. In cold-rolled plate specimens (Fig. 3(b)), particles containing Al, Mn, and Fe were detected, and particles containing only Al and Mn, thus indicating the presence of both Al-Mn-Fe and Al-Mn intermetallic compounds in the alloys. Al-Mn-Fe intermetallic compounds similar to those of the casting alloy were detected on the surfaces of the cold-rolled plate specimens; however, the morphologies of these surface particles differed considerably from those observed in the casting alloy specimens, with diameters ranging up to 10 µm. These Al-Mn-Fe and Al-Mn intermetallic compounds were (89.3-90.0)at%Al-(7.4-8.5)at%Mn-(2.2-2.7)at%Fe and (93.7-95.1)at%Al-(4.9-6.3)at%Mn, respectively, regardless of potential. Dissolution at the surfaces of the Al-Mn-Fe intermetallic compounds was also



(a) Casting alloy

Fig. 3 FE-SEM images of the Al-1.5%Mn (a) casting alloy and (b) cold-rolled plate surfaces obtained after constant-potential electrolysis in EmImCl-AlCl₃ at potentials of 0.2, 0.4, 0.6, and 1.0 V, a charge density of 30 C cm⁻², and a temperature of 323 K.

10 µm

observed at potentials above 0.6 V. In contrast, dissolution at the edges of the Al-Mn intermetallic compounds was seen at 1.0 V.

Next, the anodic dissolution and cathodic deposition behaviors (i.e., the electrorefining behavior) of the Al-1.5%Mn alloy were investigated at a higher electric charge density (100 C cm⁻²). Photographs of the Al-1.5%Mn anodes and Cu cathodes after constant-potential electrolysis at potentials of 0.2, 0.6, and 1.0 V are shown in **Fig. 4**. At 0.2 V, the surface of both the

10 µm



Fig. 4 Optical photographs of the Al-1.5%Mn casting alloy and cold-rolled plate anodes and a Cu cathode after constant-potential electrolysis in EmImCl-AlCl₃ at potentials of 0.2, 0.6, and 1.0 V, a charge density of 100 C cm⁻², and a temperature of 323 K.

alloy anodes became dark, with the casting alloy exhibiting more discoloration than the cold-rolled plate. However, at 0.6 V, the surface discoloration after electrolysis was reduced. At 1.0 V, the cathode surface exhibited a smoother morphology after electrolysis, and dendritic electrodeposits were observed.

The XRD measurement results for the Al-1.5%Mn casting alloy and cold-rolled plates before and after constant-potential electrolysis (0.2 V, 100 C cm⁻²) are shown in Fig. 5. The obtained XRD patterns of both specimens exhibit peaks consistent with Al, $Al_6Fe_{0.5}Mn_{0.5}$, Al_6Mn , or $Al_{12}Mn$. For the casting alloy (Fig. 5(a)), the peak intensity of the (110) plane of $Al_6Fe_{0.5}Mn_{0.5}$ and Al_6Mn (2 $\theta = 18^\circ$) increases after constant-potential electrolysis. The peak intensity of the (220) plane of Al also increases after electrolysis, whereas those of the other Al-associated peaks decrease. For the cold-rolled plate specimen (Fig. 5(b), the peak intensities of the (110) and (135) planes of Al₁₂Mn and Al₆Mn, respectively, increase considerably after electrolysis. Conversely, the peak intensities of the (111) and (222) planes of Al decrease considerably after electrolysis, with the latter disappearing entirely. The other peaks observed in the diffraction patterns could not be clearly identified.

The Al, Mn, and Fe EDS profiles of the Al-1.5%Mn anode specimen surfaces and cross-sections after constant-potential electrolysis (0.2 V) are shown in Fig. 6. On the surface of the casting alloy (Fig. 6(a)), several areas with high concentrations of Al and Mn were detected via EDS. Linear Al-Mn-Fe intermetallic compounds were also observed across the entire surface. The surface of the cold-rolled plate (Fig. 6(b)) also exhibited high Al and Mn concentrations; however, as previously observed in the FE-SEM images (Fig. 3), the Al-Mn-Fe or Al-Mn intermetallic compounds differed considerably in morphology compared to those in the casting alloy. In the crosssection of the casting alloy (Fig. 6(c)), continuous filmlike products were observed in the surface layer (as marked by a blue square in the SEM image), which consisted of enriched Mn. These film-like products were analyzed further at high magnification (marked by a red square in the SEM image); here, several micrometer-scale layers of enriched Mn and Al-Mn-Fe intermetallic compounds were observed. The Mn composition was then determined via EDS point analysis to be 16.4% in the enriched layer (i) and 2.2% near the interface between the enriched layer and



Fig. 5 XRD patterns of the Al-1.5%Mn (a) casting alloy and (b) cold-rolled plate before and after constant-potential electrolysis EmImCl-AlCl₃ at a potential of 0.2 V, a charge density of 100 C cm⁻², and a temperature of 323 K.



Fig. 6 FE-SEM images and corresponding Al, Mn, and Fe EDS profiles of Al-1.5%Mn specimens after constant-potential electrolysis EmImCl-AlCl₃ at a potential of 0.2 V, a charge density of 100 C cm⁻², and a temperature of 323 K: (a) casting alloy surface; (b) cold-rolled plate surface; (c) casting alloy cross-section; (d) cold-rolled plate cross-section.

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Table 2 Composition of the Al-1.5%Mn specimens after constant-potential electrolysis at a potential of 0.2 V, a charge density of 100 C cm⁻², and a temperature of 323 K:
 (i)–(ii) casting alloy; (iii)–(iv) cold-rolled plate.

Analysis point	Al [mass%]	Mn [mass%]
(i)	83.6	16.4
(ii)	97.8	2.2
(iii)	89.2	10.8
(iv)	98.2	1.8

Table 3Composition of anode alloys and electrodeposits
on the cathode before and after constant-
potential electrolysis in $EmImCl-AlCl_3$ at
potentials of 0.2, 0.6 V, and 1.0 V, a charge
density of 100 C cm⁻², and a temperature of
323 K: (a) casting alloy and (b) cold-rolled plate
anode.

	Al: Mn: Fe [mass%]	
	Anode	Cathode
(a) Casting alloy		
Before	99.0:1.0:0.0	_
0.2 V	95.0:4.7:0.3	100.0:0.0:0.0
0.6 V	98.6:1.4:0.0	99.8:0.2:0.0
1.0 V	99.0 : 1.0 : 0.0	98.2 : 1.2 : 0.6
(b) Cold-rolled plate		
Before	99.0:1.0:0.0	_
0.2 V	91.2:8.4:0.4	100.0:0.0:0.0
0.6 V	99.0:1.0:0.0	99.2:0.6:0.2
1.0 V	99.0 : 1.0 : 0.0	98.4 : 1.0 : 0.6

the Al matrix (ii). These values were calculated based on the total amount of Al and Mn detected by EDS. In the cross-section of the cold-rolled plate (Fig. 6(d)), the Mn-enriched layer could no longer be observed at lower magnification (area indicated by the blue square). However, when analyzed at high magnification (area highlighted by the red square), a thin film-like product approximately 1 µm in thickness was seen. Mn was detected in this film. In addition, Al-Mn-Fe and Al-Mn intermetallic compounds were observed in the enriched layer. Similarly to the casting alloy, the Mn enriched layer (iii) and the area near the interface between the enriched layer and the Al matrix (iv) were analyzed using EDS point analysis; 10.8 and 1.8% Mn were detected in the enriched layer and near the interface, respectively. (Tables 2 and 3)

The Mn concentrations on the casting alloy and cold-rolled plate anode surfaces and in the electrodeposit on the cathode before and after constant-potential electrolysis are shown in **Fig. 7**.



Fig. 7 EDS-measured Mn concentrations in the Al-1.5%Mn (a) casting alloy and (b) cold-rolled plate anode surfaces and the cathodic electrodeposits before and after constant-potential electrolysis in EmImCl-AlCl₃ at potentials of 0.2, 0.6 V, and 1.0 V, a charge density of 100 C cm⁻², and a temperature of 323 K.

The Mn concentration was calculated relative to the percentage sum of the Al, Mn, and Fe concentrations detected via EDS. The anode surfaces were analyzed using EDS point analysis at three arbitrary areas to obtain average values for the Mn and Fe concentrations in each case. At potentials of 0.6 and 1.0 V, arbitrary areas were analyzed, while at 0.2 V, the dark areas observed in Fig. 4 were analyzed. The electrodeposits on the cathode were also analyzed at five arbitrary points. For the casting alloy (Fig. 7(a)), after electrolysis at 0.2 V, the Mn concentration on the anode surface was higher than before electrolysis, while Mn was not detected in the electrodeposit. At 0.6 and 1.0 V, the anode Mn concentration was similar



Fig. 8 The changes in the electric charge density with the current density during the constant potential electrolysis for Al-1.5%Mn cold-rolled plate anode at a potential of 1.0 V, at a charge density of 100 C cm⁻², and photographs of the anode surface at each electric charge density (a) before and after electrolysis of at (b) 1, (c) 3, (d) 5, (e) 10, (f) 20, (g) 30, (h) 100 C cm⁻².

to that before electrolysis, but Mn concentrations of 0.6 and 1.0%, respectively, were detected in the electrodeposits. For the cold-rolled plate (Fig. 7(b)), similar concentration changes were observed at both the anode and the cathode, with 0.2 and 1.2%Mn present in the electrodeposits after electrolysis at 0.6 and 1.0 V, respectively. Negligible differences in the concentration of Fe were observed between the casting alloy and the cold-rolled plate; On the anode surface, Fe concentrations of 0.3-0.4 were detected after electrolysis at 0.2 V. However, at 0.6, and 1.0 V, Fe was not detected. In the electrodeposits, Fe was not detected at 0.2 V. However, 0.1-0.2 and 0.6%Fe concentrations were detected after electrolysis at 0.6 and 1.0 V, respectively.

The change in the current density with electric charge density during constant-potential electrolysis $(1.0 \text{ V}, 1-100 \text{ C} \text{ cm}^{-2})$ with an Al-1.5%Mn cold-rolled plate anode, as well as optical photographs of the anode surfaces before and after electrolysis at each electric charge density studied, are shown in **Fig. 8**.

The graph shows that the current density reaches its maximum at an electric charge density of 5 C cm⁻²; higher charge densities result in slightly decreased current densities until a cm⁻². The anode surface also became smoother with increasing charge density (Fig. 8(a)-(h)).

To further investigate the surface changes on the anode specimens, FE-SEM images were taken after constant-potential electrolysis (1.0 V) at electric charge densities of 10, 20, and 100 C cm⁻² with additional Mn and Fe EDS analysis (**Fig. 9**). Here, the Al-Mn intermetallic compounds (Fig. 9(a)-(c)) exhibit little dissolution as the electric charge density is increased. Conversely, the Al-Mn-Fe intermetallic compounds (Fig. 9 (d)-(f)) exhibit vigorous dissolution of their surfaces with increasing charge density, resulting in a considerable reduction in particle size after electrolysis at 100 C cm⁻².

The Al, Mn, and Fe concentrations in the Al-Mn and Al-Mn-Fe intermetallic compounds on the surface of the Al-1.5%Mn cold-rolled plate anode, as measured



Fig. 9 FE-SEM images of the Al-1.5%Mn cold-rolled plate surface and the corresponding Mn and Fe EDS mappings obtained after the constant potential electrolysis in the EmImCl-AlCl₃ ionic liquid at potentials of 1.0 V for Al-Mn intermetallic compound at a charge density of (a) 10, (b) 20, (c) 100 C cm⁻², and for (d)-(f) Al-Mn-Fe intermetallic compound, and a temperature of 323 K.







by EDS point analysis, are presented in Fig. 10. Here, Al and Mn concentrations in Al-Mn and Al, Mn, and Fe in Al-Mn-Fe show little variation as a function of electric charge density.

4. Discussion

From Eq. (1), $C_{\rm Mn}$ and $\rho_{\rm SS}(T)$ values increase with Mn solid solution composition in the Al-Mn alloys. Thus, from Eq.(2), the conductivity of the Al-Mn

alloys decreased with increasing Mn solid solution composition. Additionally, for the Al-1.5%Mn alloys, the conductivity was higher in the cold-rolled plates than in the casting alloys (Fig. 1(a)). The EPMA analysis results (Fig. 1(b)) show that Al-Mn intermetallic compounds were formed in the Al-1.5%Mn cold-rolled plate but not in the casting alloy; this suggests that Mn was deposited from the solid solution into the Al matrix phase as an Al-Mn intermetallic compound via heat treatment after the casting process. It is, therefore, plausible that the conductivity of Al-1.5%Mn increased after cold-rolling because of a decrease in the amount of Mn solid solution in the Al matrix. Additionally, the EPMA analysis results show that the intermetallic compounds in the Al-Mn alloy are fine particles with diameters below 10 µm; additionally, these occupy a much smaller area on the Al-Mn alloy surface than on the Al matrix. Therefore, the Al matrix is the main conductive part, and the influence of these intermetallic phases on the electrical conductivity of the Al-Mn alloys was considered smaller than that of the Mn solid solution.

The anodic linear sweep voltammetry behaviors of the Al-1.5%Mn casting alloys and cold-rolled plates (Fig. 2(a)) were consistent with the typical pure Al dissolution behavior reported previously in EmImCl-AlCl₃ ionic liquids³⁴. In the voltammograms of Al-Cu alloys, peaks in the anodic current density are derived from intermetallic Al₂Cu¹⁴; in contrast, no such peaks were observed in the Al-Mn alloys. However, in the voltammograms obtained at different scanning rates (Figs. 2(b) and (c)), an inflection point near 50 mV, which is slightly lower than the dissolution potential of pure Mn, was observed as the scanning rate was decreased. Because this inflection point was observed in both the casting alloys and cold-rolled plates, it was considered that this characteristic arises from either the Mn solid solution or the Al-Mn-Fe intermetallic compounds in both specimens. However, as shown by the SEM images of the anode surfaces after constant-potential electrolysis (Fig. 3), dissolution of the Al-Mn-Fe intermetallic compound only occurs at potentials over 0.6 V. This indicates that the inflection point is not because of the presence of Al-Mn-Fe intermetallic compounds, but because of Mn solid solution into the Al matrix. As the dissolution potential of pure Mn is approximately 0.1 V, it is considered that at potentials below 0.1 V, Mn dissolution into the electrolyte does not occur, and Al in the matrix phase preferentially dissolves. Therefore, at these potentials, Mn solid solution in the matrix phase becomes concentrated at the Al surface, which may inhibit Al dissolution into the electrolyte and thus results in the inflection point. The observed decline in the current density between the maximum and minimum values is attributed to forming a solidified layer of electrolyte associated with an increase in the local concentration of Al ions near the anode surface³⁴⁾. Because many intermetallic compounds are present on the surface of the Al-1.5%Mn alloy, it is considered that a dense solidified layer of electrolyte does not form easily, which would decrease the anode's resistance to dissolution. Therefore, the potential of maximum current density in the voltammograms of Al-1.5%Mn increases over that of 99.999%Al, accompanied by an increase in the maximum current density. Conversely, because there are fewer intermetallic compounds on the surfaces of Al-0.5%Mn and Al-1.0%Mn, it is considered that a dense solidified layer of electrolyte that resists dissolution is easily formed. Furthermore, SEM-EDS analysis of the anode cross-section after constant-potential electrolysis (Figs. 6(c) and (d)) indicates that an enriched layer of Mn was formed at a potential of 0.2 V. This is reflected in the voltammograms of Al-0.5%Mn and Al-1.0%Mn, where the potential of maximum current density decreases below that of 99.999% Al. This arises because of simultaneous the formation of an electrolyte-derived solidified layer, which acts as a dissolution barrier, and the formation of a Mn-derived enriched layer, which are thought to reduce the current density at this potential. As Al-0.5%Mn possesses the lowest number of intermetallic compounds, it is plausible that a denser Mn-enriched layer is formed on the surface of Al-0.5%Mn than that of Al-1.0%Mn; as a consequence, the anodic voltammograms of Al-0.5%Mn is shifted to a lower potential than that of Al-1.0%Mn.

From the SEM-EDS analysis results of the crosssection of Al-1.5%Mn after constant-potential

electrolysis (0.2 V, 100 C cm^{-2}) (Fig. 6(c) and (d)), it was observed that a thicker and higher-concentration Mn enriched layer was formed on the surface layer of the casting alloy than that of the cold-rolled plate. In addition, intermetallic compounds were observed in the enriched layers. This alloy exhibited increases in the XRD peak intensities at $2\theta = 18^{\circ}$ (Fig. 5(a)) after electrolysis under the same conditions; because only the Al-Mn-Fe intermetallic compound was identified in the Al-1.5%Mn casting alloy, these diffraction peaks were attributed to the $Al_6Fe_{0.5}Mn_{0.5}$ (110) crystal plane. In the XRD pattern of the cold-rolled plate (Fig. 5(b)), the peak intensities of the (110) and (135) planes of Al₁₂Mn and Al₆Mn, respectively, increased after electrolysis. These results suggest that the intermetallic compounds did not dissolve under these electrolysis conditions; instead, the Al in the matrix phase preferentially dissolved, forming a Mn-enriched layer interspersed between the intermetallic compounds on the surface layer as it was observed that a thicker Mn-enriched layer was formed in the casting alloy than in the cold-rolled plate, which may be attributed to the higher amount of Mn solid solution in the matrix phase.

Their electrorefining behavior was clarified based on the anodic dissolution behavior results for the Al-Mn alloys. The measured Mn and Fe concentrations on the anode surface (Fig. 7) increased after electrorefining at 0.2 V; however, these elements were not detected in the electrodeposits. This further suggests that the Al-Mn-Fe intermetallic compounds did not dissolve at this potential. Because the casting alloy had a higher Mn solid solution concentration than the cold-rolled plate, the Mn concentration at the anode surface increased further in the casting alloy anode upon electrolysis. At 0.6 V, the anode surface of the casting alloy was similar in composition to that before electrolysis, while small concentrations of Mn and Fe were detected in the electrodeposit. This suggests that the dissolution of the Mn solid solution from the matrix phase and the Al-Mn-Fe intermetallic compound occurred at this potential, which could be attributed to the simultaneous dissolution of Al from the matrix phase. In the cold-rolled plate, part of the Mn solid solution in the matrix phase was converted into Al-Mn intermetallic compounds after electrolysis; thus, the increased Mn concentration in this anode surface after electrolysis at 0.6 V may arise from the presence of these compounds. Furthermore, the Mn concentration in the electrodeposit is lower for the cold-rolled alloy than that of the casting alloy; this can be attributed to the increased number of Al-Mn-Fe and Al-Mn intermetallic compounds on the surface of the cold-rolled plate. During electrolysis at 1.0 V, the matrix phase and intermetallic compounds dissolve at the same rate; thus, the concentrations of Mn and Fe on the anode surface are the same as those before electrolysis. However, the dissolution rate of the intermetallic compounds is increased at 1.0 V compared to that at 0.6 V, resulting in an increase in the concentration of Mn and Fe ions in the electrolyte. As a result, the amount of Mn and Fe co-deposited at the cathode is larger at the higher potential. As observed in the optical images of the anode surfaces after electrolysis (Fig. 4), the anode surface becomes smoother at higher potentials because of accelerated dissolution, regardless of the difference in the metallurgical structures between the casting and cold-rolled alloys. Consequently, the amounts of Mn and Fe co-deposited on the cathode were similar between the two anode types.

From the SEM-EDS results of the surfaces of Al-1.5%Mn cold-rolled plates after constant-potential electrolysis (1.0 V) at electric charge densities of 10, 20, and 100 C cm⁻² (Fig. 9), it was observed that the intermetallic compounds dissolved as the electric charge density was increased. However, the surface morphology of the Al-Mn-Fe intermetallic compounds changed more drastically than that of Al-Mn, particularly at a charge density of 100 C cm⁻². This suggests that Al-Mn intermetallic compounds are more resistant to electrolysis-induced dissolution than Al-Mn-Fe. Furthermore, from the elemental analysis of the Al-Mn and Al-Mn-Fe intermetallic compounds after electrolysis at various electric charge densities (Fig. 10), negligible changes were observed in the elemental composition as the electric charge density was increased. This suggests that when the Al-Mn-Fe and Al-Mn intermetallic compounds dissolve, Al, Mn, and Fe diffuse into the electrolyte at equivalent rates.

Based on the interpretation of the results described above, an illustration of the proposed anodic



Fig. 11 Schematic diagrams of the anodic dissolution for (a) the casting alloy and (b) cold-rolled plate anodes in the EmImCl-AlCl₃ ionic liquid.

dissolution mechanisms of the casting and cold-rolled Al-Mn alloys are shown in Fig. 11. Such changes in the dissolution behavior of metallurgical structures have been previously reported during anodization in sulfuric acid solutions^{35), 36)}. In acidic conditions, Al and Mn dissolve as Al(III) and Mn(II), respectively³⁵; however, during anodization in sulfuric acid, Al-Mn intermetallic compounds do not dissolve and are included in the anodized film³⁶⁾. However, in EmImCl-AlCl₃ ionic liquids, because the anodic dissolution behavior changes depending on the applied potential and electric charge density, in addition to the differences between the metallurgical structures, the reaction mechanisms involved were not previously identified. In this study, these complex dissolution mechanisms have been clarified for the first time. At potentials below 0.2 V, Al in the matrix phase preferentially dissolves and a Mn-enriched layer is formed on both alloys, thus preventing the dissolution of Mn in the electrolyte. Also, Al-Mn-Fe or Al-Mn intermetallic compounds are not dissolved at this potential. Thus, Al is preferentially electrodeposited on the cathode. However, at higher potentials, Mn solid solution in the matrix phase and Mn or Fe in the intermetallic compounds dissolve in the electrolyte, thus resulting in co-deposition on the cathode.

Additionally, it was observed in this study that the difference in the dissolution potential between pure Al and pure Mn was small (approximately 0.1 V). In contrast, the presence of several metallurgical structures in the Al-Mn alloys, which are more difficult to dissolve into the ionic liquid than Mn solid solutions, results in decreased rates of co-deposition of

Mn onto the cathode during the electrorefining process.

This implies that the range of anodic potentials where high-purity Al can be obtained by electrorefining is expanded when using intermetallic compound-comprised Al-Mn alloys as anodes. Thus, the electrorefining process can be improved by reducing the amount of Mn solid solution in the matrix phase and promoting the precipitation of Al-Mn intermetallic compounds via heat treatment after the casting process. Combining these controls on the metallurgical structure and anodic dissolution potential of Al-Mn alloy anodes allows the dissolution of Mn into the electrolyte to be suppressed, thus enhancing the purity of electrorefined Al.

5. Conclusion

In this study, the anodic dissolution behavior of Al-Mn alloys in an EmImCl-AlCl₃ ionic liquid was investigated. The obtained results are summarized as follows:

- During linear sweep voltammetry of Al-1.5%Mn alloy, an inflection point of the current density derived from Mn solid solution in the matrix was shown near 50 mV vs. Al/Al(III) as the scanning rate was slowed.
- In the constant potential electrolysis of Al-1.5%Mn casting alloy and cold-rolled plate, Al in the matrix phase preferentially dissolved at a potential of 0.2 V, and an enriched layer derived from Mn solid solution in the matrix phase was formed on the surface layer. The Mn-enriched layer was thicker in the casting alloys with a higher solid solution.
- Dissolution of the Al-Mn-Fe intermetallic compounds and the Al-Mn intermetallic compounds occurred at potentials higher than 0.6 V, and 1.0 V. Dissolution of these intermetallic compounds was facilitated by increasing electric charge density.
- Mn was co-deposited with Al on the cathode at potentials where Mn solid solution in the matrix phase and intermetallic compounds containing Mn dissolved.

From these results, a mechanism for anodic dissolution in Al-Mn casting and cold-rolled alloys has been presented, whereby the combined effect of low dissolution potential and the presence of robust intermetallic compounds prevents the co-deposition of impurities during the electrorefining of Al, thus increasing the efficiency of the reclamation process. This development is anticipated to inform future efforts into improving Al recycling processes and further reduce the environmental and energy costs of Al manufacturing.

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