Dissolution Characteristics of Al-Si Alloys in AlCl₃-NaCl-KCl Molten Salt at 423 K
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Al-Si alloy plate (anode)

Al(III)

Al(III)

Al(III)

Al(III)

AlCl₃-NaCl-KCl molten salt (423 K)

Cu plate (cathode)
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ABSTRACT

Herein, the dissolution behaviors of Al–Si casting alloy and cold rolled alloy anodes in AlCl₃-NaCl-KCl molten salt were investigated at 423 K to produce high-purity Al from Al-Si alloys. All the Al-Si alloys were purified to more than 99.4 wt% by electrorefining. In particular, the purity of the AC4C and Al-11%Si alloys was 99.9 wt% each. It was confirmed from linear sweep voltammetry (LSV) measurements that anodic dissolution did not occur in the Si molten salt electrolyte. The dissolution of Al occurred preferentially on the anode surface of the ADC12 alloy during electrolysis, while the undissolved Si formed an enriched layer on the surface. In the ADC12 and AC4C casting alloys, a microstructure identical to that of the bulk metal was observed on the surface after electrolysis. On the contrary, the Si microstructure in the cold-rolled Al-11%Si alloy was fine, and adhesion was weak and did not remain firmly on the surface. In addition, the Si-enriched layer on its surface did not significantly affect the outcome of the 50-h electrorefining experiment.

Keywords: Electrorefining, Molten salt, Anodic dissolution, Al-Si alloy
1. Introduction

Al alloys are widely used because of their high specific strength and excellent corrosion resistance. In the recycling of used Al alloys, the production of recycled Al ingots by mixing and melting with new Al ingots is the mainstream process. The energy required for this process is approximately 3% of the energy used when the Hall–Heroult process is employed. This mainstream recycling process is known as “cascade recycling” because various alloying elements are mixed in each time the recycling is repeated, thus decreasing the quality. The process does not remove the alloying additive elements, but only readjusts the concentrations where a low quality is acceptable, hence, the resulting material is often used as a raw material for Al casting alloys and die casting. However, this process results in the generation of non-recyclable levels of low-grade Al alloys, which are disposed of in landfills.

Currently, Japan is entirely dependent on overseas imports for Al. Hence, it is necessary to develop technologies for producing high purity Al from Al alloys that are difficult to recycle. Additionally, a Japanese society must be established wherein Al is domestically recycled as much as possible. Al-Si alloys are widely used owing to excellent heat and wear resistance. However, Si, an alloying element, is difficult to remove during recycling. Generally, Al-Si casting alloys contain many alloying additive elements, and casting is the only manufacturing process. Consequently, compounds within the alloy exist with a coarse microstructure. In contrast, Al-Si cold-rolled alloys have fewer alloying elements, and the manufacturing process is repeated from casting to rolling. Thus, the compounds in the alloy are crushed and dispersed, resulting in a fine microstructure.

Electrorefining using a molten salt is an effective method to upgrade recycling in Al–Si alloys. Many studies have reported the electrodeposition of Al alloys using molten salts, and these studies have been particularly aimed at electrorefining. However, only a few studies have compared Al-Si alloys of different microstructures. In a chloride molten salt, the lowest melting point of the AlCl₃–NaCl–KCl system is 366 K, which is relatively low. The electrodeposition of Al using the AlCl₃–NaCl–KCl molten salt was investigated in previous studies. This study aims at electrorefining using this molten salt as an electrolyte at a relatively low temperature and by utilizing lesser energy. Moreover, a limited number of studies are available on the dissolution behavior of alloys employed as anodes during electrorefining using molten alloys. Cold-rolled and casting Al-Si alloys differ in terms of their Si concentration and microstructure. Hence, in this study, effects of the differences in the Si concentration and microstructure between cold-rolled alloys and casting alloys, which are used as anodes in electrolysis, on electrorefining were examined. The cross-sections of the anodes after electrorefining were observed, and the electrodeposits on the cathodes were analyzed. Furthermore, the dissolution mechanism of the Al-Si alloys was discussed based on the results for the dissolution behavior of pure Si.
2. Experimental

2.1 Preparation of the electrolyte

A mixture of AlCl$_3$ (Kanto Kagaku Co., Ltd., 98.0%), NaCl (Sigma-Aldrich, 99%), and KCl (FUJIFILM Wako Pure Chemical Corporation, 99.5%) at a molar ratio of 61:26:13 was used as the molten salt in this study. NaCl and KCl were dried in a vacuum at 393 K for 24 h before mixing. The molten salt was then melted in a glass vessel at 423 K in the air atmosphere. A three-electrode cell was used for electrochemical measurements, and a schematic illustration of the electrochemical cell is shown in Fig. 1. A glass vessel of 150 mL with a 5 cm diameter was used for the electrochemical cell. A cylindrical aluminum alloy covered with glass wool was placed on the outside of the cell to maintain a constant temperature. The cell that attached the electrodes was an Al alloy or a Cu plate set in a polytetrafluoroethylene (PTFE) holder, maintaining an inter-electrode distance of 2 cm. A PTFE sealing tape regulated the electrode surface (1 × 2 cm). The anode and cathode were fixed with a PTFE plate (8 cm diameter) as the cell lid and connected to a potentiostat (HZ-7000, Hokuto Denko Co., Ltd.). The temperature of the electrolyte was maintained at 423 K on a hot plate.

2.2 Linear sweep voltammogram (LSV) measurement

An Al plate (Nilaco Corp., 99.999 %) and Si plates of the n-type (Nilaco Corp., Low 100, <0.02 Ω) and p-type (Nilaco Corp., Low 100, <0.02 Ω) were used as the working electrodes. These plates were ultrasonically cleaned with acetone for 10 min. A Cu plate (Nilaco Corp., 99.96 %) was used as the counter electrode. An Al wire (Nilaco Corp., 99.99 %) was used as the reference electrode. The linear sweep voltammogram was measured in the AlCl$_3$–NaCl–KCl molten salt at 423 K in the potential range from 0 V to 1.2 V with a scan rate of 5 mV s$^{-1}$.

2.3 Electrorefining experiment

Three types of Al-Si alloys were selected: an ADC12 alloy (82.8 wt% Al–10.6 % Si–2.8 % Cu–1.3% Fe–0.9% Zn), which is a casting alloy with a relatively high Si concentration of approximately 11 wt%; an AC4C alloy (90.2 wt% Al–7.4 % Si–0.6 % Mn–0.5% Fe), and a cold-rolled Al–11%Si alloy with Si concentration similar to that of the ADC12 alloy. The alloy samples were supplied by UACJ Corporation, and their respective Al and Si compositions are listed in Table 1. The alloy specimens were polished by a water-resistant SiC paper from #220 to #600 and ultrasonically cleaned with acetone for 10 min. Subsequently, the specimen and pure Cu plate (Nilaco Corp., 99.96 %) were placed in the PTFE holder as the anode and cathode, respectively. An Al wire (Nilaco Corp., 99.99 %) was set in the PTFE lid as the reference electrode. The electrorefining experiment of the Al-Si alloys was conducted in the AlCl$_3$–NaCl–KCl molten salt at 423 K at a constant current density of 10 mA cm$^{-2}$ for 50 h.
After electrorefining, the anode and cathode were washed using pure water and subsequently dried. The composition of the electrodeposits on the cathode was analyzed by X-ray fluorescence spectroscopy (XRF, XGT-9000, Horiba Co., Ltd.). The surface morphology of the anode was observed using scanning electron microscopy (SEM, JSM-6010PLUS/LA, JEOL), and the elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDS, JSX-3100R2, JEOL). The compounds were identified by X-ray diffraction (XRD, BRUKER, D2PHASER, Cu-Kα radiation). The anode was embedded in a cold resin, cut, and then mirror finished to observe the cross-section of the anode. The cross-section was also analyzed elementally by electron probe microanalysis (EPMA, JXA-8100, JEOL).

3. Results

3.1 Linear sweep voltammogram (LSV)

The LSV measurements of Al and Si were measured in AlCl₃–NaCl–KCl molten salt at 423 K. The corresponding LSV curves are shown in Fig. 2. The dissolution current density of Al increases linearly with increasing potential. The n- and p-type Si samples showed no increase in the dissolution current density with a potential shift to toward the noble side. Their LSV curves appeared to almost overlap on the horizontal axis and showed very small values over the measured potential range. The current densities of the n- and p-type samples at 1.2 V are 28 μA cm⁻² and 13 μA cm⁻², respectively.

3.2 Purity of electrorefined Al

The changes in the anode and cathode potentials with time during the electrorefining of the ADC12 alloy are shown in Fig. 3. The cathode potential was almost constant. However, the anode potential gradually increases with time; consequently, the electrolysis voltage between the anode and cathode also increases. A similar increasing voltage trend during electrolysis is also observed for the AC4C and Al–11%Si alloys. The concentration of Al and Si in the electrodeposits at each cathode is illustrated in Table 2. All the alloys exhibited an Al purity of more than 99% due to electrorefining. The observed purity is significantly improved compared to that of the Al concentration in the alloys before electrolysis. A comparison of the Si concentration before and after electrolysis reveals decreases of approximately 1/50 and 1/360 for ADC12 and Al–11%Si, respectively. These results suggest that the electrorefining method is a promising for efficiently removing Si from Al alloys. In addition to Si, Fe and Cu are also detected as impurities in electrorefined aluminum at the cathode from the ADC12 alloy anode.

3.3 Anode surface after electrorefining
The surface changes in the three Al-Si alloys before and after electrorefining are shown in Fig. 4. The metallic luster on the surfaces of each alloy is lost, and the color has changed to dark gray after electrorefining. In the ADC12 and AC4C casting alloys, relatively large irregularities are formed on the surface. In the cold-rolled Al-11%Si alloy, the surface appears dark gray immediately after electrolysis. However, because of the weak adhesion of the surface formations, they are washed away with pure water, resulting in a surface similar to that before electrorefining. The concentrations of Al and Si on the three types of the anode surfaces after electrorefining are listed in Table 3. The Si concentration on the different anode surfaces has increased compared to that before electrorefining, indicating that these surfaces are enriched by Si. Therefore, the dark gray surface has high Si content. The dark gray material of the Al-11%Si alloy that was washed away with pure water was also collected. The XRD analysis revealed the presence of Si, suggesting that a Si enriched thin layer was also formed on the cold-rolled alloy surface.

### 3.4 Observation of the anode cross-section

The cross-sectional SEM images and EDS mappings of the three Al-Si alloys are shown in Fig. 5; where figures (a) and (b) are images for casting alloys, and (c) is the image for cold-rolled alloy. The SEM images of the casting alloys demonstrated the formation of a surface layer with many gaps on the bulk alloy. The Al profile indicates the presence of Al in this surface layer, with a concentration much lower concentration than that of the bulk alloy. The Si profile suggests the presence of a large amount of Si on the surface layer. In addition, the Si concentrations in these alloys are similar to that of the base alloy. These results reveal that the surface layer formed after electrorefining is mainly composed of Si. The casting alloys in images (a) and (b) exhibited different Si morphologies depending on the concentration. A needle-like structure is observed in (a), while a mesh structure was observed in (b), which depended on the concentration. However, the SEM images of the cold-rolled Al–11%Si alloy showed almost no surface layers compared to those observed in (a) and (b). Comparing the Si profiles of (a), (b), and (c), Si is uniformly dispersed in the Al-11%Si alloy, whereas it is unevenly scattered in the ADC12 and AC4C alloys, with the presence and absence of certain areas.

The minute amounts of Fe and Cu in the electrodeposit on cathode of electrorefining of ADC12 alloy with electrolysis time for 50 h were detected by EPMA. The SEM image and elemental profiles by EPMA are illustrated in Fig. 6. The SEM image of (a) shows the bulk alloy and surface layer on the right and left, respectively. The Al and Si profiles in (b) and (c), respectively, indicate similar results to those in Fig. 5. The Fe and Cu in (d) and (e), respectively, are observed in the bulk alloy and surface layer, and a similar dispersion is observed in both. These results indicate that the dissolution reaction at the anode is mostly Al, with no involvement from Si, Fe, and Cu.
3.5 Comparison of XRD patterns before and after electorefining

Figure 7(a) shows the XRD patterns of the surface of the ADC12 alloy anode surface before electorefining and of the generated surface layer after electorefining. Before electorefining, the Al peaks at approximately 38°, 45°, 65°, 78°, and 82° are strongly visible, and the Si diffraction peaks at approximately 29°, 48°, 56°, 69°, 77°, and 88° are weak compared to the Al peaks. However, only Si diffraction patterns are in the pattern of the alloy surface after electrolysis, while the Al diffraction patterns disappeared. In addition to Si and Al\textsubscript{7}Cu\textsubscript{2}Fe show peaks at approximately 22° and 43°, while Al\textsubscript{2}Cu shows a peak at approximately 42°. The XRD patterns of the AC4C (Fig. 7(b)) and Al-11%Si (Fig. 7(c)) alloys also showed similar results. In the AC4C alloy, the weak intensity of the Si diffraction peaks before electrolysis also increases at all positions after electrolysis. The peak at 2θ = 36° is consistent with the diffraction pattern of AlCu. For Al-11%Si, the Si(111) peak intensity at 2θ = 28° increases after electrolysis, while the intensity of other Si diffraction peaks decreases. In the diffraction pattern of Al, the intensities at 38° and 45° corresponding to the (111) and (200) planes decreased after electrolysis.

4. Discussion

High purity Al was electrodeposited from the Al-Si alloy anodes by electorefining. The trace amounts of Fe and Cu detected as impurities in the electrodeposited layer on the cathode in the electorefining of the ADC12 alloy are unlikely to have anodically dissolved, considering the dissolution potential at the anode. However, Fe and Cu may be anodically dissolved depending on the potential change during electrolysis, considering that these impurities formed intermetallic compounds with Al. It has been reported that the Si in Al alloys is anodically dissolved and electrodeposited at the cathode in high-temperature molten salts at 1023 K.\textsuperscript{10} Huan et al. reported the progressive dissolution of Si for the same AlCl\textsubscript{3}-NaCl-KCl molten salt electrolyte,\textsuperscript{21} however, in the present study, LSV measurements and electorefining results for molten salt at the 423K revealed no anodic dissolution of Si. Fine black particles were found at the bottom of the electrochemical cell after electorefining, which were found to be crystalline Si from XRD measurements. Therefore, it is possible that the Si detected at the cathode was physically detached from the remaining Si at the anode surface, moved to the cathode surface by the convection of the electrolyte, and incorporated into the electorefined Al.

As shown in the cross-sectional profiles in Figs. 5 and 6, Al, which is the matrix phase, in the three Al-Si alloys preferentially dissolves in the anodic dissolution reaction, whereas Si and other metal components remained in a porous form on the surface without dissolving. However, the Al on the surface of the porous layer observed in the SEM image is not dissolved anodically and is considered to have a different microstructure compared to that of the matrix Al. The Al concentration in this area is low and is detected at the exact location as Si. Furthermore, no diffraction patterns of Al are observed in the XRD illustrated in Fig. 7. Thus, this microstructure may be a solid solution with Si.
Comparing Figure 5(a) and (b), different shapes of the porous surface layers were formed after electorefining, although they are from the Al-Si casting alloys. It is concluded that the different Si concentrations in the alloys results in different microstructures constituting the base alloys, and the Si distribution is directly reflected in the porous layer on the surface. The Si distribution of Al alloys, a cold-rolled alloy, is made fine and uniform by the cold-rolled process during production. Immediately after electorefining, the surface appeared black, which was cleared by washing with water in order to clean the electrolyte. This black surface is attributed to the fine shape of the surface layer formed during electorefining, which is similar to the Si distribution of the base alloy. Consequently, the surface layer exhibited low adhesion, and was washed away with pure water.

During the dissolution at the anode via electorefining, the Al dissolution progressed preferentially. Hence, a Si enriched layer of was formed, which remained on the surface without dissolving. Thus, this layer could have resisted Al dissolution to gradually increase the potential, as shown in Fig. 2(a). However, because of its porous structure, this surface layer did not offer significant resistance to Al leaching from the internal matrix phase and insignificantly affected the 50-h electorefining process insignificantly. The surface layer formation at the anodes of Al-Si casting and cold-rolled alloys revealed in this study may not affect the dissolution reaction of Al even at longer electorefining durations.

5. Conclusion

The electorefining of the casting and cold-rolled Al-Si alloys as anodes was performed, and the dissolution behavior of each alloy surface was investigated from the surface and cross-section after electorefining. The following results were obtained.

1. In LSV results revealed that the anodic dissolution of Al occurred easily, whereas that of Si rarely occurred.
2. In the all Al-Si alloys, Si-enriched layer was formed on the anode surface because Al preferentially dissolved from the alloy. Over 99.4 wt% of Al was electrodeposited at the cathode from the all Al-Si alloy anodes.
3. Due to the electorefining process, the Si-enriched layer remained on the surface of the casting alloys after washing. However, in the cold-rolled alloy (Al-11%Si), the Si structure was finely crushed during the rolling process. Thus, even if the Si-enriched layer was formed, its adhesion would be weak.
4. The cross-sectional observation of the Si-enriched layer indicated that it was structured with many crevices. Therefore, this layer was not significant resistance to the dissolution of Al from the bulk during the 50-h electorefining experiment.
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Figure and Captions

**Table 1.** Al and Si concentrations in the three alloys used in this study.
**Table 2.** Concentrations of the Al and Si electrodeposits on the cathode after electrorefining.
**Table 3.** Concentrations of Al and Si at the anode after electrorefining.

**Figure 1.** Schematic illustration of the electrochemical cell and photographs of the anode (left) and the cathode (right) placed in the polytetrafluoroethylene holder.

**Figure 2.** Linear sweep voltammmograms of (a) pure Al (b) n-type Si, and (c) p-type Si.

**Figure 3.** Potential and voltage changes with time during electrorefining of the ADC12 alloy: (a) potential of the working electrode and (b) potential of the counter electrode.

**Figure 4.** Photographs of the anode of before and after electrorefining, (a) ADC12 alloy, (b) AC4C alloy, and (c) Al-11%Si alloy.

**Figure 5.** Cross-sectional scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental profiles of Al and Si in the alloy anodes after electrorefining: (a) ADC12 alloy, (b) AC4C alloy, and (c) Al-11%Si alloy.

**Figure 6.** Cross-sectional observation of the ADC12 alloy anode after electrorefining, (a) SEM image, and electron probe microanalysis (EPMA) mapping analysis of (b) Al, (c) Si, (d) Fe, and (e) Cu.

**Figure 7.** XRD patterns of the anode before and after electrorefining, (a) ADC12, (b)AC4C, and (c)Al-11%Si alloys.
Table 1

|         | Al (wt%) | Si (wt%) |
|---------|----------|----------|
| ADC12   | 82.8     | 10.6     |
| AC4C    | 90.2     | 7.4      |
| Al-11%Si| 89.2     | 10.7     |
|       | Al (wt%) | Si (wt%) |
|-------|----------|----------|
| ADC12 | 99.4     | 0.23     |
| AC4C  | 99.9     | 0.05     |
| Al-11% Si | 99.9 | 0.03     |
Table 3

|       | Al (wt%) | Si (wt%) |
|-------|----------|----------|
| ADC12 | 22.2     | 60.7     |
| AC4C  | 63.5     | 31.7     |
| Al-11% Si | 79.9 | 19.8     |
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7