Effects of Fe, Si, and Cu on Recrystallization Behavior in High Purity Aluminum Foil

T YAMANOI

Aluminum Rolled Products Division, SHOWA DENKO K.K., Sakai, Osaka, Japan

Abstract. The correlation between the recrystallization behavior of high purity aluminum foil, which is used as the electrode material of electrolytic capacitors, and the influence of Fe, Si, and Cu contents on the formation of recrystallization texture was systematically investigated. The following results were obtained: (1) Room-temperature recrystallization, which occurs during cold rolling of the highest-purity material, was suppressed by adding approximately 10 mass ppm of Fe, Si, and Cu. The effect was strongest for Cu, followed by that for Si and Fe. (2) The main component of texture after the final heat treatment changed in the order {001}<100>→{011}<411>→{126}<411>→{123}<412> as the purity of the aluminum foil decreased. In particular, {126}<411> was an characteristic orientation for extremely coarse grains and was considered to have originated from the rolling texture (β-fiber). This coarse grain growth was considered to be related to the decrease in the growth rate of the recrystallized grains depending on the purity of the matrix.

1. Introduction

In the high purity aluminum foil in electrolytic capacitors, which is one of the main applications of high purity aluminum foil, the control of grain size and texture in terms of electrostatic capacity and bending strength is one of the objectives of material design. Fe, Si, and Cu content is known to influence this phenomenon [1][2][3], but the effects on recrystallization behavior in very small amounts of other elements have not been identified. In this study, a considerable amount of coarse grains, which are obtained at temperatures slightly above room temperature, was observed. The study aimed to investigate the respective effects of Fe, Si, and Cu on recrystallization behavior and to clarify its growth process.

2. Experimental Procedures

2.1. Samples

The chemical composition of the sample used in this study is shown in Table 1. The sample preparation process is shown in Fig. 1. Samples was casting in book molds for aluminum slabs. The sample was hot-rolled at a starting temperature of 793 K and air-cooled afterwards. Samples that were heat-treated after hot rolling were dipped in the salt bath at 723 K, held for 600 s, and water-cooled immediately afterwards. The rolling reduction ratio between each pass was maintained within the range of 30±10% during the cold rolling and the temperature of the sample was kept from rising.

2.2. Observation and analysis method

The microstructure was observed using a polarizing microscope, after the sample had been polished with emery paper, buffed, and anodized through treatment with Barker's solution. The hardening and softening behaviors of the specimens that exhibited recrystallization were evaluated using Vickers hardness and tensile tests. Texture was analysed via pole figure measurement using X-ray diffraction (XRD) and via electron backscattered diffraction (EBSD) measurement using FE-SEM.
3. Experimental Results

3.1. Softening behavior during cold rolling

Some of the samples in this study recrystallized during cold rolling. For example, Fig. 2 shows the microstructure and {111} pole figure after the cold rolling of the A1 composition sample in Table 1. Figure 2 shows a microstructure whose recrystallization is almost complete and the pole figure has a very sharp cube texture.

Figure 3 shows the results obtained upon evaluating the hardening after cold rolling to 0.1 mm thickness using Vickers hardness test. In the sample shown in Fig. 3, elements other than the composition concentration plotted on the abscissa are equal to or less than 2 mass ppm, indicating the influence of Fe, Si, and Cu only. Figure 3 shows that Cu content inhibits softening by only 5 atom ppm (11 mass ppm) in aluminum in the no-annealing sample after hot rolling, and that the inhibiting effect in the order of Si and Fe is attenuated. Figure 3(b) shows that Vickers hardness for cold-rolled foils annealed after hot rolled sheets increased holistically compared to that of the no-annealed foils. This is attributable to the reduction of the initial dislocation density by the annealing of the hot-rolled sheets, and the insufficiency of the total strain for recovery and recrystallization during cold rolling. However, no tendency was observed in the A4, A6, and A11 samples containing Fe only. Further, the order of Vickers hardness of foils was reversed in no-annealing and annealing samples of the hot rolled sheets containing a large amount of Fe. Researchers in a previous study on work softening in the system added only Fe to a high purity aluminum base [4]; therefore, the lattice defects may have disappeared as a result of the precipitation of Al-Fe intermetallic compounds on lattice defects such as dislocation cells, subgrain boundaries, and recrystallized grain boundaries. Based on these results, Fe is considered to slightly contribute to the increase in the recrystallization temperature for matrix aluminum, and acceleration of recrystallization by precipitation during heat treatment is thought to have an impact on this phenomenon. [5]

Table 1. Chemical compositions of the specimens (mass ppm)

| Specimen | Si (mass ppm) | Fe (mass ppm) | Cu (mass ppm) | Al (mass ppm) |
|----------|---------------|---------------|---------------|---------------|
| A1       | 2             | 1             | 2             | Bal.          |
| A2       | 2             | 1             | 11            | Bal.          |
| A3       | 10            | 1             | 2             | Bal.          |
| A4       | 2             | 12            | 2             | Bal.          |
| A5       | 11            | 12            | 2             | Bal.          |
| A6       | 1             | 21            | 2             | Bal.          |
| A7       | 10            | 10            | 10            | Bal.          |
| A8       | 9             | 10            | 15            | Bal.          |
| A9       | 10            | 11            | 24            | Bal.          |
| A10      | 12            | 11            | 49            | Bal.          |
| A11      | 2             | 52            | 2             | Bal.          |

Fig. 1. Production and experimental process of samples.

Fig. 2. Grain structure and texture after cold rolling. [001] <100>
3.2. Effect of Fe, Si, and Cu on microstructure after final heat treatment

Figure 4 shows the microstructure and the {111} pole figure when the cold-rolled foils (0.1 mm thickness) were heated at 473 K without heating of the hot-rolled sheets.

![Microstructure and Pole Figure](image)

**Fig. 4.** Effect of Fe, Si, and Cu on grain structure and texture after final annealing. No annealing after hot rolling, final annealing conditions: 473 K × 7.2 ks

- [001]<100>
- [123]<412>
- [011]<411>
- [126]<411>
Figures 4(a), (b), and (c) show that the Fe, Si, and Cu contents had individual effects on the microstructure and texture respectively. Figure 4(a) A5 exhibited a remarkably well-developed cube texture \{001\}<100>. However, the main orientations of Figs. 4(b) A3 and (c) A2 were not only cube texture but also the orientation components near \{011\}<411>, which were intermediate between the Goss \{011\}<100> and brass \{011\}<211> orientations. Before final annealing, Fig. 4(b) represented the partial recrystallization, Fig. 4(c) represented the working structure, and the result illustrated in Fig. 3 was considered. In the case of Figs. 4(b) and (c), the growth of the cubic texture \{001\}<100> was suppressed; thus, the orientation developed from the rolling texture (s-orientation\[6\], \beta-fiber\[7\]).

Figures 4(d), (e), and (f) show the effect of the amount of Cu at the approximately 10 mass ppm level of both Si and Fe. In sample Fig. 4(d) A5 (Cu: 2 mass ppm), relatively coarse recrystallized grains with a crystal grain size of more than 200 μm developed almost uniformly. The pole figure confirmed the existence of the cube texture \{001\}<100> and an almost \{011\}<411> texture was observed in Figs. 4(b), (c). Next, mixed structures of extremely coarse recrystallized grains (hereafter referred to as huge grains) and un-recrystallized regions, which extended in the rolling direction of sample (e) A7 (Cu: 10 mass ppm). Based on the texture analysis, this huge grain was considered to be an orientation component near \{126\}<411>. This orientation was also identified in Fig. 4(d), so was considered to be not typical to Fig. 4(e). Further, the rolling texture of the un-recrystallized region was represented by the \{123\}<412> orientation. Finally, in Fig. 4(f) A10 (Cu: 49 mass ppm), recrystallized grains were not observed and huge grains were not also observed. In addition, rolling texture was determined based on pole figure analysis. As shown in Figs. 4(d), (e), and (f), the grain growth rate in recrystallization was considered to be related to the growth of the huge grains in Fig. 4(e) owing to a certain amount addition of Cu content. Additionally, in the samples of A8 (Cu: 15 mass ppm), huge grains were observed as Fig. 4(e), and huge grains were not observed in the sample of A9 (Cu: 24 mass ppm). Therefore, the upper threshold of Cu contents at which huge grains were expressed in this study was considered to range between 15 and 24 mass ppm.

4. Discussion

From the pole figure analysis shown in Fig. 4, the influence of Fe, Si, and Cu only on the formation of cube texture in the final annealing increased in the order of Fe < Si < Cu, and the preferred orientation of texture changed from \{001\}<100> to \{011\}<100> + \{011\}<411>. Moreover, in the estimated 10 mass ppm samples of Si and Fe, the preferred orientation changed from \{001\}<100> to \{123\}<412>, which is thought to have stemmed from the rolling texture (\beta-fiber), and grain growth was remarkably high in the process.

Figure 5 shows the tension softening curves of samples with different contents of Cu, and approximately 10 mass ppm level of Si and Fe contents. This image shows that softening began to increase in speed at 333 K in the samples of A5 and 433 K in the samples of A7. To investigate the orientation relationship between recrystallized grains and the surrounding matrix, samples of (x)A5 (annealed at 343 K for 4.2 ks) and samples of (y) A7 (annealed at 443 K for 7.2 ks) were produced, and EBSD analysis was carried out. The results are shown in Fig. 5. The IPF MAP, KAM MAP, and ODF were applied to the respective samples through EBSD analysis.

First, recrystallization was considered to be completed in the blue region where deviation of crystal orientation from adjacent regions was very small from KAM MAP, and the grains and orientations were confirmed from IPF MAP. Then, the region where the recrystallization was considered to be proceeding to the surrounding matrix was selected (inside the square frame in Fig. 6), and finally, ODF analysis in this region was carried out.
Fig. 6. Typical inverse pole figure map (IPF MAP), kernel average misorientation map (KAM MAP), and orientation distribution function (ODF) of coarse-grained specimens. (x) A5: after 343 K × 7.2 ks annealing, (y) A7: after 443 K × 7.2 ks annealing.
Based on the ODF analysis shown in Figure 6, the preferred orientation of the recrystallized grain in sample (x) was \{001\}<100> and \{113\}<273> in sample (y). Figure 7 shows the angles between the face azimuth obtained from the region adjacent to the recrystallized grain and the face azimuth of the recrystallized grain. Figure 7 shows that the deviation angle of the crystal orientation with recrystallized grains adjacent to recrystallized grain \{011\}<100> of sample (x) was relatively small from approximately 4° to 27°. And the deviation angle of the crystal orientation from the adjacent un-recrystallized region was approximately 21° to 74°, which was large, albeit with some variation. Next the region adjacent to the \{113\}<273> grains of sample (y) was the un-recrystallized region in the observation range, and the deviation angle of the crystal orientation was mainly within the range of 35° to 45°. In this analysis, the identification of common axes of rotation showing a coincidence relationship \(^{[8]}\) in the region with the deviation angle in Fig. 7 was not accomplished. However, in sample (y), wherein remarkably grain growth had occurred, the un-recrystallized region showed a clear anisotropy of crystal orientation and development of the huge grains in the rolling direction. Therefore, it was inferred that the preferred grain growth had occurred.

5. Conclusion

In this study, high purity aluminum foils with varying Fe, Si, and Cu contents and processes were analyzed using the XRD/pole figure and the SEM/EBSP method. Based on the results, we discussed the influence of Fe, Si, and Cu content on the formation of a coarse grain texture. The results are summarized as follows:

1. Room-temperature recrystallization, which occurs during the cold rolling of the highest-purity material, was suppressed by adding several ppm of Fe, Si, and Cu. The effect was strongest for Cu, followed by Si and Fe.
2. The main component of texture after the final heat treatment changed in the order \{001\}<100>→\{011\}<411>→\{126\}<411>→\{123\}<412> as the purity of aluminum foil decreased.
3. In this study, extremely coarse recrystallized grains were observed in samples wherein the Si and Fe contents were both approximately 10 mass ppm and the Cu content was within a certain range. The preferred orientations of these huge grains were \{126\}<412>, \{113\}<273>, etc., which were inferred to be the preferred growth from the rolling texture (β-fiber).

Acknowledgments

The author would like to thank Dr. M. Sakaguchi for the opportunity to begin this study, and Prof. H. Inoue for their advice on the measurement and analysis of texture. This study was supported by SHOWA DENKO K.K. and their members.

References

[1] Miki I and Warlimont H 1968 Z. Metallkdke. 59 408-414
[2] Henmi Z and Nagai T 1967 J. Japan Inst. Metals 31 329-333
[3] Nagahama K and Miki I 1970 J. Japan Inst. Light Metals 20 137-144
[4] Ohno Y and Nakamura H 1977 Aluminium 53 539-542
[5] Sakaguchi M, Yamanoi T and Hasegawa M 1987 Z. Metallkdke. 78 80-86
[6] Inoue H 2015 Mater. Trans. 56 61-69
[7] Inoue H 2001 Materia Japan 40 589-591
[8] Kronberg M L and Wilson F H 1949 Metals trans. 185 501-514