Effect of Homogenization on Recrystallization and Precipitation Behavior of 3003 Aluminum Alloy

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This investigation studies 3003 aluminum alloys for automobile heat exchangers. The effects of precipitation in homogenization treatments, recrystallization in extrusion and brazing on extrusion forming ability and final material properties are examined. At first, fine second phase particles were precipitated during the 460°C × 9h homogenization treatment and coarse particles were precipitated by homogenization treatments with 600°C × 9h. Second, when the precipitation were not plentiful and fine enough during extrusion, the amount of solution dominated the extrusion breakout pressure, and recrystallization was easier; on the contrary, the domination state was replaced by plentiful and fine precipitated particles, and recrystallization became more difficult. Additionally, the hardness after extrusion was lower in the complete recrystallization position, and higher in the incomplete recrystallization position. Finally, in brazing, the sample under the 460°C × 9h condition (a) underwent full recrystallization from partial recrystallization with a reduction in strength; the local position of the edge of the sample under the 600°C × 9h → 460°C × 3h condition (c) exhibited a second recrystallization and a significant drop in hardness.

Keywords: 3003 aluminum alloy, homogenization, precipitation, extrusion, brazing, recrystallization, second recrystallization

1. Introduction

Light automobile heat exchangers with excellent performance have become increasingly important in recent years owing to the growing demand for saving energy. Consequently, efficient fin-tube heat exchangers are entering the mainstream. Its tubes are usually produced by extruding 3003 aluminum alloys, and are then combined with fins via brazing bonds at 600°C for 10 minutes. Therefore, studying the effects of all manufacturing processes, including homogenization, extrusion and brazing, on each other, is very valuable.

Gray Al₆(Mn,Fe) particles tend to precipitate during low-temperature homogenization; black α-Al₁₂(Mn,Fe)₃Si particles tend to precipitate at high temperature, and gray Al₆(Mn,Fe) particles are redissolved by increasing the temperature or extending the duration of homogenization treatment. Many studies about such homogenization have been published.1–4) Most of the literature has focused on the rolling in 3000-series aluminum alloy because it is widely used to make beverage containers.5–9) Some studies have also discussed the feasibility of precipitation hardening by heat treatments.10,11) Among these works, T. Doko and S. Asami undertook the more correlative ones5,6) about this investigation. They indicated that a plentiful fine particulate precipitate or a large amount of solution inhibited recrystallization. However, homogenization, extrusion and even brazing of automobile heat exchangers manufacture process have not been closely studied.

Although increasing the strength of 3000-series aluminum alloy by final heat treatments is difficult, the precipitation and redissolution behaviors can occur during extruding and brazing at various temperatures to vary the strength of the final products. Accordingly, in this investigation, various homogenization conditions were applied to control the shape and the distribution of second phase precipitated particles, and the effects of these conditions on the extrusion and the brazing were determined. Extrusion would be stopped half way to obtain more explicit information.

2. Experimental

The alloy used was of composition JIS A 3003. Table 1 presents the composition of the studied ingots. The ingots were homogenized under four conditions: condition (a) 460°C × 9h, condition (b) 600°C × 9h, condition (c) 600°C × 9h + Step 460°C × 3h, and condition (d) 460°C × 1h + Step 600°C × 9h. All heating rates and cooling rates were 50°C/h, and the ingots were water-quenched to room temperature. After all of the processes had been completed, the microstructures of the samples were observed by OM and TEM. Their electrical conductivities were also examined.

Figure 1 presents all of the experimental processes. After homogenization, extrusion was performed with a rod-shaped die, a preheating temperature of 450°C, an extrusion ratio of 26.7 and a ram speed of 8 mm/s; the extrusion pressure was recorded using a computer. The extruded rod material was quenched into water to room temperature soon after extrusion. Extrusion was stopped half way and the samples observed by TEM to elucidate the change in the microstructure. Finally, the samples were made from the extruded rod material to simulate brazing treatment at 600°C for 30 minutes and then each observation and test was conducted.

With regard to the experimental apparatus and set up, a JEOL-JEM-3010 TEM was used with an accelerating voltage was 200 kV. TEM samples were made by electropolishing test pieces at −25°C by jet polishing. The samples whose

| Table 1 Chemical composition of the specimen (mass%). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Si   | Fe   | Cu   | Mn   | Al   |
| 0.1  | 0.5  | 0.12 | 1.09 | bal. |
3. Result and Discussion

3.1 Effect of homogenization treatment on solution and precipitation

AA3003 aluminum alloys are not heat-treatable. Mn atoms that are dissolved in an aluminum matrix can produce a strain field to obstruct the movement of electrons. Therefore, electrical conductivity of a large quantity of solution is low, and that of a small one is high. Table 2 presents the electrical conductivities after casting and four homogenization treatments. The amount of precipitation was larger with less solution after homogenization under conditions (a) and (c) because their electrical conductivities were both much higher than that after casting; the conductivity under condition (b) or (d) was only slightly higher than that after casting, indicating that precipitation was less and the quantity of solution was greater. In step-homogenization, electrical conductivity was determined by the last temperature, so the sample precipitated again at the end of the application of 460°C × 3 h, condition (c), and dissolved again probably at the end of the application of 600°C × 9 h, condition (d). Overall, solid-solution strengthening was significant under conditions (b) and (d) after homogenization at 600°C, and feeble under conditions (a) and (c) with a last temperature of 460°C.

Figure 2 presents OM image of the precipitation after homogenization under four conditions. Fine second phase particles were precipitated during 460°C × 9 h homogenization treatment, and coarse particles were precipitated during other three homogenization treatments with 600°C × 9 h. Number densities of these three conditions were very approximate. The TEM image in Fig. 3. verified that gray and black precipitation of various sizes and complex shapes were precipitated by low-temperature homogenization under condition (a); black precipitation were precipitated with a similar size and spheroidal shapes under high-temperature homogenization, condition (b). The results that the gray precipitation were relatively unstable Al$_{6}$(Mn,Fe) particles and that the black ones were relatively stable $\alpha$-Al$_{13}$Mn$_{7}$Fe$_{3}$Si particles support the results in the literature. Step-homogenization yielded all of the particle characteristics obtained under low-temperature and high-temperature homogenization: in the last step at 460°C × 3 h under condition (c), since the sample tended to exhibit heterogeneous precipitation on second phase particles precipitated at the beginning of the 600°C × 9 h step, the particles became larger, and the precipitation density changed slightly. The rectangular particles and two-colored particles were also formed for these reasons. This result corresponded to the paper that had been announced by S. Asami and T. Doko. In their report, the density of second phase particles precipitated under the condition of 600°C × 9 h → 475°C × 81 h was close to that under 600°C × 9 h. Although the duration of the last step was such longer than ours, the results still supported with each other. Furthermore, in the study of T. Minoda and H. Yoshida, heterogeneous precipitation may appear infrequently in the last step of 500°C × 10 h, since the sample had been homogenized in the first step of 630°C × 10 h and precipitated rarely. While under condition (d), the variation in electrical conductivity between the two steps of was such close (first step was 38.8% and last step was 38.6%) that the approximate solution quantities between the two steps were determined by the incomplete precipitation in the first step at 460°C × 1 h with the short treatment time. Some of the finer, smaller and more unstable second phase particles precipitated in the first step at 460°C × 1 h, redissolving via an Ostwald ripening mechanism into the aluminum matrix at the end step at 600°C × 9 h, and the larger and more stable particles continued to grow into spheroids. Therefore, diversiform

<table>
<thead>
<tr>
<th>Condition</th>
<th>Conductivity (IACS%)</th>
<th>As-cast</th>
<th>Homogenization</th>
<th>Extrusion</th>
<th>Brazing</th>
<th>Extrusion breakout pressure, $\sigma_0$/kgf/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 460°C × 9 h</td>
<td>37.8</td>
<td>43.0</td>
<td>42.4</td>
<td>38.7</td>
<td>81.9</td>
<td></td>
</tr>
<tr>
<td>(b) 600°C × 9 h</td>
<td></td>
<td>39.0</td>
<td>39.2</td>
<td>39.1</td>
<td>83.6</td>
<td></td>
</tr>
<tr>
<td>(c) 600°C × 9 h → 460°C × 3 h</td>
<td>39.0</td>
<td>42.4</td>
<td>41.9</td>
<td>39.6</td>
<td>78.2</td>
<td></td>
</tr>
<tr>
<td>(d) 460°C × 1 h → 600°C × 9 h</td>
<td>38.8</td>
<td>38.6</td>
<td>38.9</td>
<td>38.8</td>
<td>84.8</td>
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</table>
precipitated particles were detected in the sample under condition (d), and the density declined to that under condition (b).

3.2 Effect of solution and precipitation on extrusion and brazing

Table 2 also presents the data of electrical conductivity after extrusion, as well as the extrusion breakout pressure. The test result of electrical conductivity after homogenization was the opposite of that of the extrusion breakout pressure. Since more precipitation and less solution resulted in weaker solid-solution strengthening under homogenization conditions (a) and (c), with higher electrical conductivity, the extrusion breakout pressure (condition (a) was 81.9, (c) was 78.2 kgf/cm$^2$) was lower. Conversely, solid-solution strengthening under homogenization conditions (b) and (d) was significant with lower electrical conductivity, and that resulted in the higher extrusion breakout pressure (condition (b) was 83.6, (d) was 84.8 kgf/cm$^2$). Besides, although the quantity of solution was lower under conditions (a) and (c), the extrusion breakout pressure under condition (a) substantially exceeded that under condition (c). The greater precipitation hardening and higher extrusion breakout pressure under conditions (a) were suspected to be related to its more and finer precipitated particles, as shown in Fig. 2. For the same reason, the extrusion breakout pressure under condition (a), with more and finer precipitated particles, was only a little lower than under conditions (b) and (d) with greater solid-solution strengthening. Additionally, the lowest extrusion breakout pressure under condition (c) was associated with the weaker solid-solution strengthening and precipitation hardening. Hence, when the precipitated particles were sparse and coarse, the quantity of solution dominated the extrusion breakout pressure. However, when the precipitated particles were plentiful and fine enough, the quantity of solution did not dominate powerfully.

Figure 4 presents OM image of recrystallization after extrusion. The direction of observation was parallel to the extrusion direction. The samples under conditions (b), (c) and (d) that had been treated at 600°C × 9 h were fully recrystallized from their edges to their centers, and the grains were very many and small. Moreover, the recrystallized grains nearer the edges of the three samples were more plentiful and smaller than those nearer the centers. Under the low-temperature homogenization condition (a), the recrystallized grains were much fewer and larger than the others, the wrought organization and the partial recrystallization also existed together in the center of the sample. These character-
istics differed markedly from those under the other three conditions.

Figure 5 presents TEM image of the plastic deformation area near the die gate before extruding out the gate. The subgrains were present in all of the samples whose OM images were the wrought organization here that was deformed from the original grains. The dislocations introduced here by plastic deformation were verified to have already recovered forming subgrains and the stored energy did not suffice to drive the recrystallization. Under condition (a), the subgrain boundary was limited by the abundant and fine second phase precipitated particles and could not expand completely. Furthermore, since the movement of the dislocations was also limited by those particles, they aggregated extensively and became entangled with each other, forming the deformation bands. Hence, the recrystallization was more difficult and resulted in the partial recrystallization after extrusion, shown in Fig. 4(a): a large amount of stored energy was introduced again when the material was extruded through the die gate, and then this stored energy caused the subgrains to break under the influence of precipitated particles. However, this energy still did not suffice to cause full recrystallization. Accordingly, dynamic recrystallization and dynamic recovery occurred together, causing simultaneous partial recrystallization and wrought organization after extrusion. Under the other three conditions with 600 °C × 9 h, fewer and sparser precipitated particles caused the weaker limitation phenomenon, and the formation of subgrains was promoted, forming more, finer ones. These also made the full recrystallization form after extrusion. In conclusion, recrystallization was more difficult when second phase precipitated particles were plentiful and fine than when they were coarse and sparse. The result also corresponded to that in the literatures. Additionally, the result that higher quantity of solution went against the generation of recrystallization was reported in the literature. However, the phenomenon was unobvious in our condition (b) and (c) with similar density of precipitated particles and different quantity of solution. More abundant, sufficient quantity of deformation and driving force of recrystallization that was introduced during extrusion may make this situation occur. Figure 6 presents the TEM image of the extruded samples. Since no subgrain was observed, the image may have been of a recrystallized part. Numerous dislocations and the limitation phenomena associated with the precipitated particles were also found here. These were the main features of dynamic recrystallization. Furthermore, the most dislocations under condition (a) corresponded to the severest limitation phenomenon associated with more and finer precipitated particles.

Fig. 3 Transmission electron micrograph (TEM) image of the precipitation after homogenization under four conditions. (a) 460 °C × 9 h, (b) 600 °C × 9 h, (c) 600 °C × 9 h → 460 °C × 3 h, (d) 460 °C × 1 h → 600 °C × 9 h.
Table 2 also presents the electrical conductivity after brazing. The electrical conductivities under conditions (a) and (c) after brazing decreased to the level after homogenization with a last step at 600°C. Since the samples under conditions (a) and (c) had been homogenized in a last step at 460°C, more unstable second phase precipitated particles easily redissolved into the aluminum matrix during brazing treatment at 600°C. The production of many dislocations during the extrusion process facilitated the diffusion of Mn atoms, so that although the brazing time was only ten minutes, the unstable particles redissolved to arrive in the grade of quantity of solution at 600°C. Under conditions (b) and (d) following homogenization at 600°C in the last step, which was also the brazing temperature, the precipitated particles were more stable, and most did not redissolve, so the electrical conductivity did not vary significantly.

Figure 7 presents the recrystallized structure after brazing. Only recrystallization under conditions (a) and (c), with substantially reduced electrical conductivity were associated with the huge variation of recrystallization. The sample under condition (a) exhibited full recrystallization from the original partial recrystallization. Recrystallization became thus easier in brazing treatment at 600°C, and so could have been driven by the stored energy that had previously been introduced. Additionally, the limitation on recrystallization by the second phase precipitated particles was much weakened by the redissolution of these particles into the aluminum matrix. Although the brazing time was only ten minutes, all of the wrought organization exhibited complete recrystallization. Under condition (c), huge grains were present near the local

![Fig. 4 Optical microstructure image of extrusion recrystallization under four homogenization conditions. (a) 460°C × 9 h, (b) 600°C × 9 h, (c) 600°C × 9 h → 460°C × 3 h, (d) 460°C × 1 h → 600°C × 9 h.](image-url)
position of the edge of the sample and most of second phase precipitated particles that were close to the edge redissolved after brazing, as shown in Fig. 7(c). In order to reduce the interface energy, some boundaries of the fine recrystallization at the edge of the sample moved suddenly, swallowing up neighboring grains, and thus growing rapidly, while the unstable precipitated particles redissolved into the aluminum matrix. Some huge grains were produced by this mechanism, called second recrystallization. Under conditions (b) and (d), the slight growth of the recrystallized grains at the edge of the sample was also caused by the decline in the interface energy. However, the insignificant variation in their electrical conductivity indicated that perhaps only exceedingly few precipitated particles redissolved under brazing treatment, so the second recrystallization did not occur.

3.3 Mechanical properties and change in recrystallization between extrusion and brazing

Figure 8 schematically models the recrystallization behavior during extrusion and brazing treatment. The precipitated particles determined recrystallization during extrusion shown in Fig. 8(a) and (b): the second phase particles precipitated at 460°C (low temperature, condition (a)) were more and finer, inhibiting the motion of dislocations and the subgrain boundaries. Therefore, its nucleation free energy of recrystallization was higher than the three other homogenization conditions with the sparser and fewer precipitated particles. Moreover, the driving force of recrystallization was the stored energy obtained by introducing the dislocations during extrusion. The deformation of each extruded rod sample was large nearer the edge, declining toward the center. When the
second phase precipitated particles were more plentiful and finer, as under condition (a), the stored energy that was introduced in the edge of the sample exceeded the nucleation free energy of recrystallization, and was a little lower than that in the center of the sample. Hence, dynamic recrystallization ran to completion at the sample edge; dynamic recovery and dynamic recrystallization occurred together at the sample center, causing partial recrystallization with effective strain hardening, which made the hardness became more unstable and higher, as shown in the Fig. 9(i). Rougher and larger edge recrystallization grains were obtained with the stored energy that only slightly exceeded the nucleation free energy of recrystallization, producing less recrystallization nuclei. Additionally, the samples with sparse and few precipitated particles occurred full recrystallization because of the stored energy that was introduced by extrusion exceeded the nucleation free energy of recrystallization throughout the samples. The full recrystallization consumed the dislocations and the stored energy, so the strain hardening was futile. Consequently, the hardness distribution plotted in Fig. 9(i) was more uniform and lower than that at the center of the sample under condition (a). Beside, more and finer recrystallization grains formed at the sample edge because the stored energy markedly exceeded the nucleation free energy of recrystallization under these conditions, producing many recrystallization nuclei. And the recrystallization grains were coarser and larger in the sample center because the stored energy only slightly exceeded the nucleation free energy there.

The partial recrystallization at the sample center under
condition (a) which yielded the most plentiful and finest precipitated particles, proceeded to full recrystallization at a high brazing temperature of 600°C. The significant drop in the hardness at the center of the sample after brazing, as shown in Fig. 9(ii), was associated with the consumption of the residual dislocations and stored energy. Furthermore, the condition (b), (c), (d) with sparser and fewer precipitated particles were distinguished into two kinds of situations: one was the redissolution of few precipitated particles and another was the redissolution of plentiful ones. The samples homogenized at 600°C under conditions (b) and (d) in the last step made difficult redissolution during brazing at 600°C, so the recrystallized grains grew only slightly, and the drop in hardness after brazing was less. Under condition (c), with the quantity of solution of 460°C, the second recrystallization of the sample was caused by the sudden removal of the
abundant recrystallization grain boundaries at the sample edge by the redissolution of many unstable second phase precipitated particles. The hardness was significantly reduced, as plotted in Fig. 9(ii).

Figure 10 compares the tensile strength and yield strength after extrusion and brazing. Since the edge of the extruded rod material was removed by lathing, according to the ASM gage of the tensile test sample, the affection brought by the variation of this organization in the edge of the sample could not be performed. However, the strength was largest under condition (a) after extrusion because the organization at the center was wrought organization. And although partial recrystallization continued to full recrystallization significantly reducing the strength after brazing treatment, the strength was still greatest under condition (a). Under conditions (b) and (d) with the last step at 600°C × 9h, the similar solution and precipitation resulted in the almost same strength of extruded samples. Moreover, the lack of growth of the recrystallization grains was associated with a lower drop in the strength after brazing. Under condition (c), the strength of the extruded sample was the weakest because few, sparse second phase particles precipitated, and the solid-solution strengthening was low. Additionally, since the edge second recrystallized part of the sample under condition (c) was removed by lathing, the strength measured here could not perform the affection of the phenomenon. Hence, the strength tested only fell very slightly as that under conditions (b) and (d). However, the second recrystallization substantially reduces the hardness of the edge of the sample, so the tensile strength and the yield strength of the integral rod sample may have been markedly reduced.

4. Conclusions

The results of obtained one may be summarized as follows. (1) The extrusion breakout pressure was determined by competition between the second phase precipitated particles and the solution of Mn atoms after different homogenization treatments: when the precipitated particles were coarse and sparse, the extrusion breakout pressure was dominated by the solution quantity. However, when the precipitated particles were plentiful and fine enough, the quantity of solution did not dominate powerfully.

(2) Recrystallization affected the hardness after extrusion: hardness was lower at positions of complete recrystallization and higher at positions of incomplete recrystallization. Moreover, the second phase precipitated particles affected the recrystallization capacity: recrystallization was more difficult when precipitated particles were plentiful and fine than when they were coarse and sparse.

(3) After brazing treatment, the sample at 460°C × 9h, condition (a), exhibited full recrystallization with a
drop in strength; areas of the edge of the sample under the 600°C × 9 h condition (c) underwent second recrystallization because of the redissolution of abundant second phase precipitated particles, significantly reducing hardness.

Fig. 9 (i) Hardness test from the edge to center of the samples after extrusion under four homogenization conditions. (ii) Hardness test from the edge to center of the samples after brazing under four homogenization conditions.

Fig. 10 Comparison of tensile and yield strength after extrusion and after brazing under four homogenization conditions. (a) 460°C × 9 h, (b) 600°C × 9 h, (c) 600°C × 9 h → 460°C × 3 h, (d) 460°C × 1 h → 600°C × 9 h.

REFERENCES