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EFFECT OF ANNEALING CONDITIONS IN AS-CAST AND Zr ADDITION ON RECRYSTALLIZATION BEHAVIOR IN Al-Mn ALLOY FIN STOCKS

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ABSTRACT

In an Al-Mn alloy heat exchanger fin stock, the effect of annealing conditions for as-cast and 0.1%Zr addition on recrystallization behavior is investigated using metallurgical analysis. Refinement of post-brazed recrystallized grains in fin stocks with Zr addition are suppressed for long-time annealing. In 0.1%Zr fin stocks, there was a decrease in the number of fine α-Al(Mn,Fe)Si dispersoids for pinning of subgrain and grain boundary. In addition, relatively homogeneous distribution of Al_3Zr dispersoids was observed with increasing annealing time in as-cast. Homogeneous distribution of Al_3Zr dispersoids can have a major effect on pinning of subgrain and grain boundary during brazing heat treatment. The homogenous distribution of fine dispersoids prior to brazing heat treatment is effective in causing the suppression of refinement of post-brazed recrystallized grain structure in aluminum alloy fin stocks.

KEYWORDS

Recrystallization, Al_3Zr, α-Al(Mn,Fe)Si, Heat exchanger, Fin stocks

INTRODUCTION

Al-Mn based alloys are widely used as fin stocks in automotive heat exchangers because of their superior mechanical properties, brazeability, sagging and so on. In particular, coarsening of recrystallized grain structure is beneficial to avoid erosion, and achieve excellent sagging resistance (Lee, Yoon, Kim & Jung, 2002). For resisting grain coarsening, the alloys should contain a dense and homogeneous distribution of fine dispersoids to retard recrystallization (Humphyreys & Hatherly, 2004). It has been demonstrated that addition of Zr to Al-Mn alloys can shift recrystallization to higher temperatures because of the distribution of fine Al_3Zr dispersoids in matrix (Pokoba, Cieslar & Lacaze, 2012). According to Tohma, Asano and Takeuchi (1987), coarsely recrystallized grain structure was obtained in 3003 alloy with Zr addition after heat treatment. However, fine Al_3Zr dispersoids are usually heterogeneously distributed because of segregation during casting and low diffusion rate of Zr in aluminum. Therefore, a homogeneous distribution of Al_3Zr dispersoids can be achieved through long-time precipitation annealing (Jia, Hu, Forbord & Solberg, 2008).

The continuous casting process is one of the most effective processes for coarsening of post-brazed grain structure in aluminum alloy fin stocks. Continuous cast Al-Mn alloy fin stocks have good strength and brazeability (Kokubo, Anami, Teramoto, Teshima & Toyama, 2015). Thus, brazeablilty can be further improved through the distribution of fine Al_3Zr dispersoids in continuous cast Al-Mn alloy fin stocks. The aim of this paper is to examine the effect of annealing conditions in as-cast and Zr addition on recrystallization behavior after the brazing heat treatment of Al-Mn alloy fin stocks that simulate continuous casting.

EXPERIMENTAL PROCEDURE

The chemical compositions of the alloys in this study are given in Table 1. The Al-Mn alloys, which are both 0 mass%Zr (0%Zr) alloy and 0.1 mass%Zr (0.1%Zr) alloy, were continuous cast to thin strips. To consider the effect of annealing conditions in as-cast, the as-cast 0%Zr and 0.1%Zr strips were heated to 450°C for 3 h or 10 h and then cooled to room temperature prior to cold rolling. Following annealing in as-cast, the strips were cold rolled to a thickness of 0.20 mm prior to intermediate annealing. To find optimum intermediate annealing condition, Vickers hardness after each temperature's annealing was measured. Intermediate annealing was performed at 450°C for 2 h to fully annealed on the as cold rolled sheets at 0.20 mm thickness, because of same temper condition being associated with same final cold rolled reduction in the fin stocks. Following intermediate annealing, samples were cold rolled to a final thickness of 0.10 mm as fin stocks. The brazing process of the automotive heat exchanger was simulated by heating the fin stocks at 600°C for 3 min. Following brazing heat treatments, the recrystallized grain structure was observed. The distribution of dispersoids was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations. Energy dispersive X-ray spectroscopy (EDX) was used to investigate the chemical composition of the dispersoids. The amounts of Mn and Zr solute in the aluminum matrix was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) after chemical extraction in phenol.

Table 1. Chemical composition of the alloy (mass%)

	Si	Fe	Cu	Mn	Zr
0%Zr	0.15	0.50	0.02	1.06	-
0.1%Zr	0.15	0.50	0.02	1.06	0.10

RESULTS

Softening Curve During Intermediate Annealing

Figure 1 shows the softening behavior with intermediate annealing on the cold rolled 0%Zr and 0.1%Zr sheets at 0.20 mm thickness, which were annealed in as-cast at 450°C for 3 and 10 h, respectively.

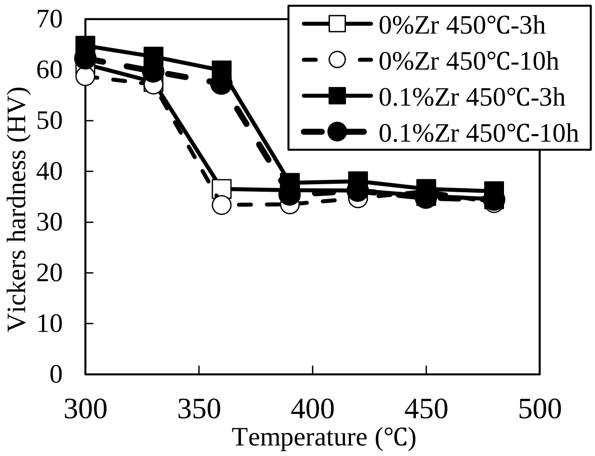


Figure 1. Softening behavior during intermediate annealing in 0%Zr and 0.1%Zr fin stocks

Zr addition dominated the softening behavior. The hardness of the 0.1%Zr sheets, which was regardless of the annealing in as-cast, significantly dropped off at 390°C. On the other hand, 0%Zr softening was at more than 360°C. It was assumed from the behavior that the intermediate annealing at more than 390°C could lead all sheets to the fully annealing being attributed to the completed recrystallization after intermediate annealing. Based on the softening behavior as shown in Figure 1, intermediate annealing was applied at 450°C in this study to fully annealed.

Recrystallized Grain Structure After Brazing Heat Treatment

Figure 2 shows the post-brazed grain structures and grain size after brazing heat treatment of 0%Zr and 0.1%Zr fin stocks annealed in as-cast at 450°C for 3 and 10 h, respectively.

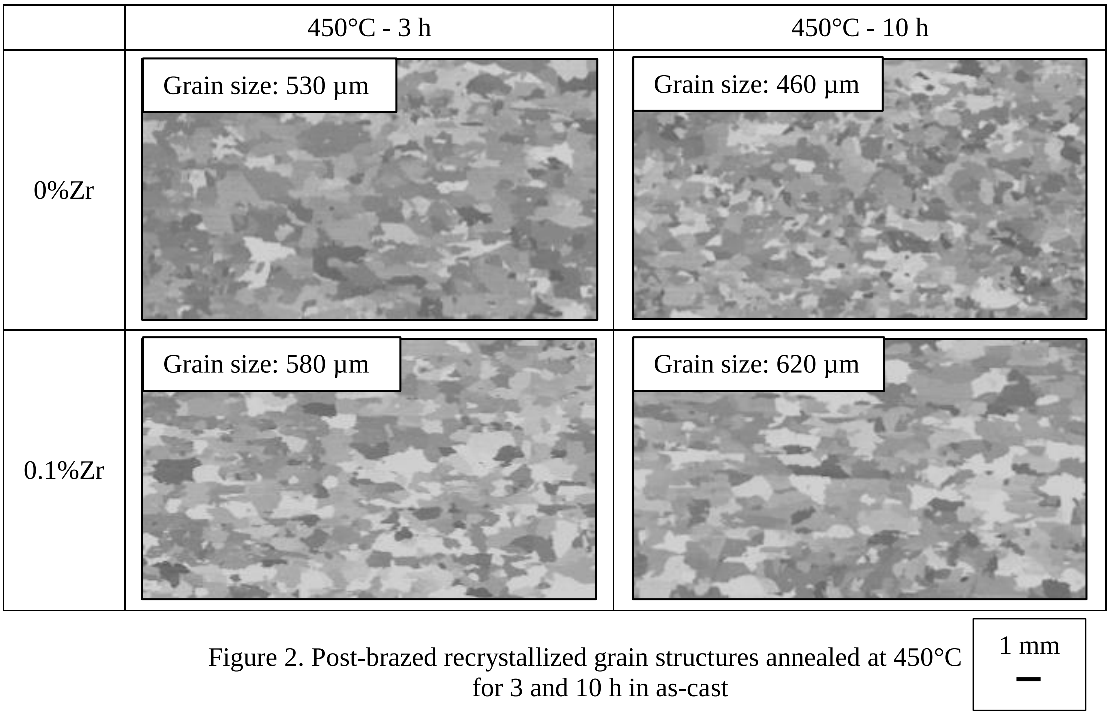


Figure 2. Post-brazed recrystallized grain structures annealed at 450°C for 3 and 10 h in as-cast

As shown in Figure 2, the all fin stocks were fully recrystallized after the brazing heat treatment. Post-brazed recrystallized grains with the 0.1%Zr addition was larger than that without Zr on each annealing time in as-cast. For 0%Zr fin stocks, post-brazed recrystallized grain size tended to decrease with increasing annealing time in as-cast. However, refinement of post-brazed recrystallized grains was suppressed in 0.1%Zr fin stocks despite the increase in annealing time in as-cast.

DISCUSSION

Effect of Secondary Particles on Recrystallization Behavior (Particle Simulated Nucleation)

In previous studies, it is clear that the recrystallization behavior was affected by (1) secondary particles (Particle Simulated Nucleation; PSN), (2) solid solute atoms in the aluminum matrix and (3) fine dispersoids (Zener-Pinning). The effect of each microstructural factors on the recrystallized grain structures as shown Figure 2 is investigated as follows. For investigation of (1) secondary particles (PSN) mechanism, the distribution of the secondary particles was observed prior to brazing heat treatment by SEM (Figure 3).

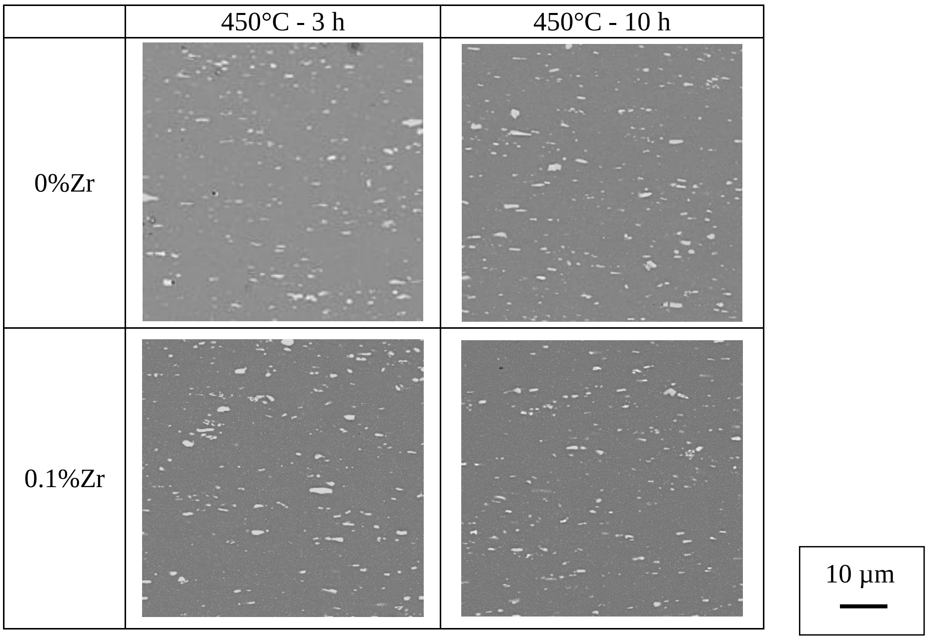


Figure 3. Distribution of secondary particles of 0%Zr and 0.1%Zr fin stocks before brazing heat treatment

The secondary particles in the aluminum matrix were almost the same size in 0%Zr and 0.1%Zr regardless of the annealing time in as-cast, and it similarly dispersed in all conditions. The EDX analysis in SEM detected Si, Fe, Mn and Al in these secondary particles. Therefore, they were mainly identified as the α-Al(Mn,Fe)Si phase. Based on the SEM images shown in Figure 3, the frequency of equivalent diameters for the secondary particles was calculated using the LUZEX analysis software. Figure 4 shows the frequency of equivalent diameters for the secondary particles.

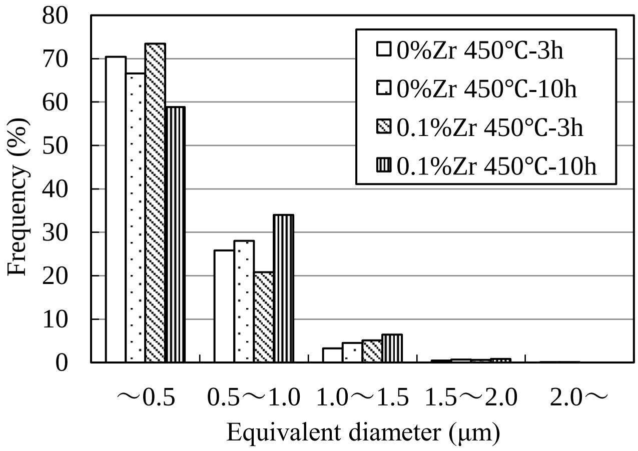


Figure 4. Frequency of equivalent diameter for secondary particles in 0%Zr and 0.1%Zr fin stocks

It was reported that large secondary particles exceeding 1 μm act as nucleation sites of recrystallization (Particle Simulated Nucleation: PSN) (Engler, Yang & Kong, 1996). As shown in Figure 4, the annealing conditions in as-cast had little effect on the frequency of equivalent diameter for large secondary particles, which was more than 1 μm, in addition, the frequency of secondary particles exceeding 1 μm was obviously lower than that of the secondary particles less than 1 μm in all fin stocks. Therefore, this result shows that a similar effect in the larger secondary particles on the recrystallized nucleation sites in all fin stocks.

Effect of Solid Solutes in Matrix on Recrystallization Behavior

With regard to solid solute atoms in the aluminum matrix, it is supposed that the solutes in the aluminum matrix would act as obstacles to dislocation migration for recrystallization in the fin stocks during brazing heat treatment. In particular, it is widely known, Mn and Zr solutes in the aluminum matrix hinder recrystallization during heat treatment (Lens, Maurice & Maurice, 2005; Hori, Saji & Kitagawa, 1973). Table 2 shows the amount of Mn and Zr solute in 0.1%Zr matrix before and after intermediate annealing based on the phenol extraction of the matrix.

Table 2. Amount of Mn and Zr solute in 0.1%Zr matrix before and after intermediate annealing (mass%)

	Mn		Zr	
	450°C - 3 h	450°C - 10 h	450°C - 3 h	450°C - 10 h
Before intermediate annealing	0.23	0.19	0.03	0.03
After intermediate annealing	0.12	0.12	0.02	0.02

The amounts of Mn solute after intermediate annealing in both 450°C for 3 and 10 h annealing were decreased to 0.12 mass% same amount, even though it before intermediate annealing were 0.23 mass% in 3 h and 0.19 mass% in 10 h. The Zr amounts before intermediate annealing for both the annealing conditions were the same, and the amount after intermediate annealing in 450°C for 3 h was also the same as it in 450°C for 10 h. The decrease in Zr amounts during intermediate annealing were insignificant. Therefore, the influence of the solute atoms on recrystallization behavior during brazing heat treatment in 450°C for 3 and 10 h was considered to be similar.

Effect of Fine Dispersoids on Recrystallization Behavior (Zener-Pinning)

Fine dispersoids of less than about 100 nm affected the recrystallization behavior because they exert a drag force on the movement of subgrain boundaries (Yamauchi & Kato, 1991). The additional precipitation of dispersoids during brazing heat treatment is unlikely to occur because the amount of the

Mn and Zr solutes in matrix after intermediate annealing was small, as shown in Table 2. Therefore, recrystallization behavior during brazing heat treatment would attribute to the distribution of fine dispersoids that existed after intermediate annealing. Figure 5 shows the TEM images of the distribution of fine dispersoids in 0.1%Zr fin stocks following intermediate annealing, and where α-Al(Mn,Fe)Si and Al_3Zr dispersoids were detected by the TEM-EDX.

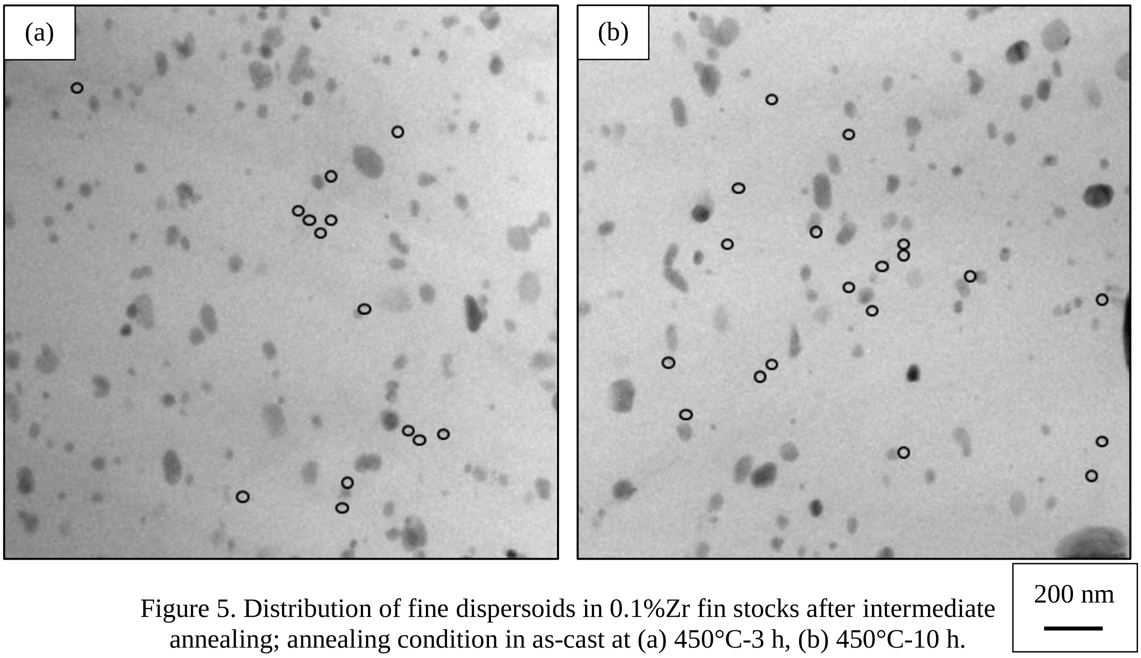


Figure 5. Distribution of fine dispersoids in 0.1%Zr fin stocks after intermediate annealing; annealing condition in as-cast at (a) 450°C-3 h, (b) 450°C-10 h. Black circles indicate Al_3Zr dispersoids

In the fin stocks, annealed in as-cast at 450°C for 3 h, Al_3Zr dispersoids were unevenly distributed, and the annealed condition had the lower Al_3Zr dispersoids density in some areas. Meanwhile, more homogeneous distributions of Al_3Zr dispersoids were observed in fin stocks annealed in as-cast at 450°C for 10 h compared to the fin stocks annealed at 450°C for 3 h. Forbord, Hallem and Marthinsen (2004) reported that the high number density of Al_3Zr dispersoids were obtained in Al-Mn-Zr alloy after annealing at 450°C for 12 h. According to Jia, Hu, Forbord and Solberg (2008), homogeneous distribution of Al_3Zr dispersoids can be achieved through long-time annealing such as two-step precipitation annealing. In this study, because diffusion rate of Zr atoms in aluminum matrix is low, the longer annealing time like for 10 h at 450°C would make Al_3Zr dispersoids distribution homogenous. α-Al(Mn,Fe)Si dispersoids were homogeneously distributed in matrix regardless of the annealing condition in as-cast. No change of average quivalent diameter and morphology of Al_3Zr dispersoids was observed by annealing conditions in as-cast. Figure 6 shows the frequency of the equivalent diameter of α-Al(Mn,Fe)Si dispersoids (< 200 nm) in 0.1%Zr fin stocks after intermediate annealing.

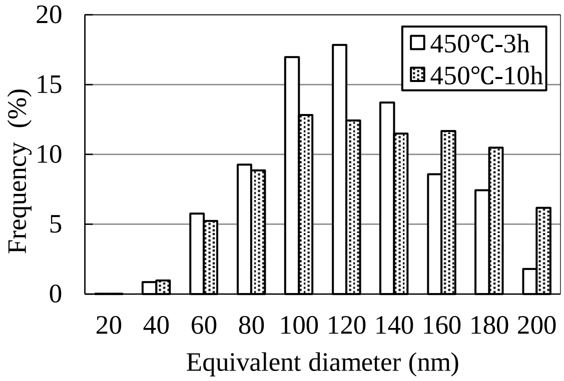


Figure 6. Frequency of α-Al(Mn, Fe)Si dispersoids in 0.1%Zr fin stocks after intermediate annealing

In the short annealing time for 3 h in as-cast, the frequency of α-Al(Mn,Fe)Si dispersoids approached the maximum in the range of 100–120 nm. By increasing the annealing time in as-cast, the number of fine α-Al(Mn,Fe)Si dispersoids of about 100 nm decreased and the distribution became broader. To investigate the effect of α-Al(Mn,Fe)Si dispersoids on recrystallization behavior, Figure 7 shows the recrystallized grain structure in fin stocks after intermediate annealing at 360°C for 2 h.

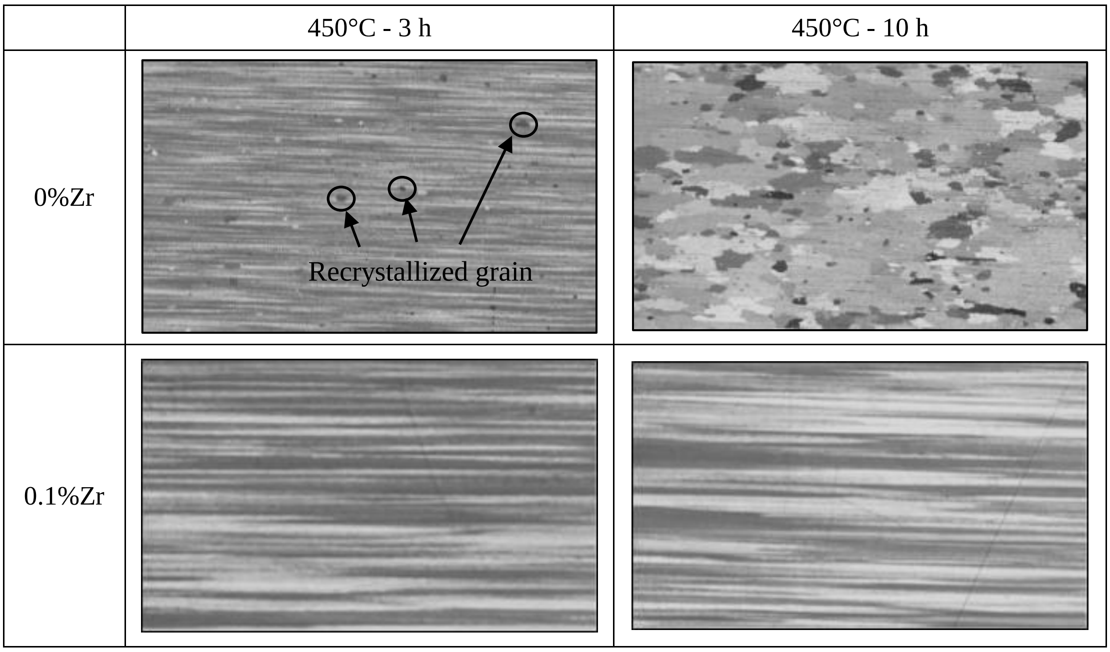
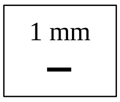


Figure 7. Recrystallized grain structure in fin stocks after intermediate Annealing at 360°C for 2 h



The 0.1%Zr fin stocks resulted in the fiber structure both 450°C for 3 and 10 h annealing conditions in as-cast. On the other hand, 0%Zr fin stocks annealed in as-cast at 450°C for 10 h was almost recrystallized, even though, the recrystallized small grains were partly found in 0%Zr fin stocks annealed in as-cast at 450°C for 3 h. There were differences in recrystallization behavior during intermediate annealing in 0%Zr fin stocks because large α-Al(Mn,Fe)Si dispersoids were already present before intermediate annealing because of long-time annealing in as-cast. Therefore, a decrease in the number of fine α-Al(Mn,Fe)Si dispersoids caused by increase of annealing time in as-cast was contribute to difference of post-brazed grain structure in 0%Zr fin stocks.

In the 0.1%Zr fin stocks, there was a decrease in the number of fine α-Al(Mn,Fe)Si dispersoids for pinning of subgrain and grain boundary, in addition, relatively homogeneous distribution of Al_3Zr dispersoids was observed with increasing annealing time in as-cast. Ryum (1969) reported that the deformed structure was preserved in the precipitate-containing (Al_3Zr) region of Al-0.5%Zr alloy after annealing at 555° C and low-density areas of precipitates were more prone to recrystallization. Similarly, in this study, high number of Al_3Zr dispersoids may act as pinning of subgrain and grain boundary. Furthermore, the recovery and recrystallization during brazing heat treatment were preferentially likely to occur in low-density areas of Al_3Zr dispersoids. Thus, by increasing annealing time in as-cast from 3 h to 10 h, the effect of α-Al(Mn,Fe)Si dispersoids on pinning of subgrain and grain boundary was considered to be less because the α-Al(Mn,Fe)Si dispersoids grew to relatively large size. In contrast to that, homogeneous distribution of Al_3Zr dispersoids would have a major effect on pinning of subgrain and grain boundary during brazing heat treatment.

CONCLUSIONS

The effect of annealing conditions in as-cast and Zr addition on recrystallization behavior during brazing heat treatment in Al-Mn alloy fin stocks was studied. The refinement of post-brazed recrystallized grains in the fin stocks with Zr addition was suppressed despite the increase in annealing time in as-cast. The influence of PSN and solid slutes in the aluminum matrix on recrystallization behavior during brazing heat treatment was small. However, difference of fine dispersoids distribution was observed with annealing conditions in as-cast. By increasing the annealing time in as-cast, the number of effiective fine α-Al(Mn,Fe)Si dispersoids for recrystallization resistance decreased. In contrast, fine Al_3Zr dispersoids were relatively homogeneously distributed in fin stocks with Zr addition with increasing annealng time in as-cast. Homogeneous distribution of Al_3Zr dispersoids would have a major effect on pinning of subgrain and grain boundary during brazing heat treatment. Therefore, these results suggest that homogenous distribution of fine dispersoids prior to brazing heat treatment is effective in causing the suppression of refinement of post-brazed recrystallized grain structure in continuous cast aluminum alloy fin stocks.

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