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Effects of Si and Zr addition on strength and recrystallization behavior of Al-Mn alloy fin stocks for automotive heat exchanger

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Abstract. For an Al-Mn alloy heat exchanger fin stocks which continuous casting was simulated in, the effects of Si and Zr addition on strength and recrystallized grain structures after brazing heat treatment were investigated. As a result of tensile test, pre-brazed tensile strength was increased with increasing Si and Zr contents in the Al-Mn alloy. On the other hands, Zr addition have a small effect on post-brazed tensile strength regardless of Si contents. This was attributed the dissolution of Al_3Zr or $(Al,Si)_3Zr$ precipitates during brazing heat treatment. Post-brazed grain structure were refined with increasing Si contents. Meanwhile, Zr addition led to larger post-brazed grain structures. It was found that Al_3Zr or $(Al,Si)_3Zr$ precipitated during intermediate annealing played to major role in retarding recrystallization during brazing heat treatment.

1 Introduction

Al-Mn alloys, having good brazeability, thermal conductivity, corrosion resistance are widely used for the fin stocks of automotive heat exchanger. Recently, thickness of fin stocks tends to decrease in order to weight reduction and miniaturization of heat exchanger. However, buckling of fin stocks more likely to occur with decreasing thickness of fin stocks. One of the main reasons for buckling is erosion in which molten filler metal diffuse into the fin stocks along grain boundaries. As a countermeasure against erosion, it is widely known that coarsening of recrystallized grain structure after brazing is effective method due to decrease of diffusion pathway. Therefore, fin stocks manufactured by continuous casting, such as twin-roll casting and twin-belt casting, are widely applied to heat exchanger. Coarsely recrystallized grain structure was obtained in twin-roll cast Al-Fe-Ni alloy after brazing heat treatment. It was considered that recrystallization of twin-roll cast Al-Fe-Ni alloys was affected less by particle stimulated nucleation (PSN) than is that of direct-chill cast Al-Fe-Ni alloys [1]. Post-brazed properties of twin-belt cast Al-Mn alloy fin stocks and Al-Fe alloy fin stocks were studied [2]. As a result, it was obvious that twin-roll cast Al-Mn alloy fin stocks have high post-brazed tensile strength and coarse recrystallized grain structure compared to Al-Fe alloy fin stocks. It has been suggested that the twin-belt cast Al-Mn alloy fin stocks have more fine dispersoids and higher amount of solute Mn in the aluminium matrix than that of Al-Fe alloy fin stocks after brazing heat treatment. It is widely known that fine dispersoids can hinder or delay recrystallization by exerting the Zener drag on moving the subgrain and grain boundaries [3]. Thus, it was supported that twin-belt cast Al-Mn alloy fin stocks have coarse recrystallized grain structure. One of the commercial Al-Mn alloys is AA3003. Maximum chemical compositions of this alloy are: 0.6wt%Si, 0.7wt%Fe. Additions of Si and Fe enhance the precipitation of $Al_6(Fe,Mn)$ or $Al_{12}(Mn,Fe)_3Si$. Furthermore, in the Zr-containing alloys, Si and Fe increase the rate of formation of Al_3Zr dispersoids, acting as catalysis [4]. Especially, addition of Si to Al-Zr alloys enhance the formation of the fine spherical Al_3Zr dispersoids and results in an increased precipitation hardening response [5]. Effect of Zr addition on sagging resistance and crystallization behaviour of AA3003 was studied [6]. As a result, coarsely recrystallized grain structure was obtained in AA3003 alloy with Zr addition after brazing heat treatment. As mentioned above, in continuous cast Al-Mn-Si alloy with Zr, recrystallized grain size and tensile strength after brazing heat treatment may be further increased.

The aim of this paper is to investigate the effects of Si and Zr addition on strength and recrystallization behaviour after brazing heat treatment of Al-Mn alloy fin stocks that simulate continuous casting.

2 Experimental

The chemical compositions of the alloys in this study are given in Table 1. In order to consider a continuous strip casting process, the Al-Mn-Si and Al-Mn-Si-Zr alloys were cold rolled to a thickness of 0.15 mm prior to intermediate annealing without homogenization and hot rolling. Intermediate annealing was performed at 400 °C for 2 h to fully annealed on the as cold rolled sheets at 0.15 mm thickness, because of same temper condition being associated with same final cold rolled reduction in

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the fin stocks. Following intermediate annealing, sheets 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.

Table 1. Chemical compositions of alloys (mass%).

Alloy	Si	Fe	Cu	Mn	Zr	Al
S15	0.15	0.50	0.02	1.06	–	Bal.
S15Z	0.15	0.50	0.02	1.06	0.10	Bal.
S8	0.80	0.50	0.02	1.06	–	Bal.
S8Z	0.80	0.50	0.02	1.06	0.10	Bal.

Pre- and post-brazed recrystallized grain structure was observed and softening behavior was investigated during brazing heat treatment by Vickers hardness. Furthermore, pre- and post-brazed tensile properties were measured. The deistribution of dispersoids was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations. Chemical composition of the dispersoids was identified by energy dispersive X-ray spectroscopy (EDS). In order to evaluate the variation of solute atoms in matrix, the amounts of Mn and Zr solute in the matrix was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) after chemical extraction in phenol.

3 Results

3.1 Tensile properties

Pre- and post-brazed tensile properties of fin stocks are shown in Table 2.

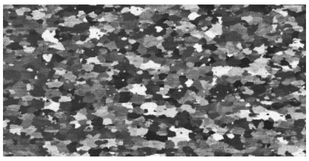
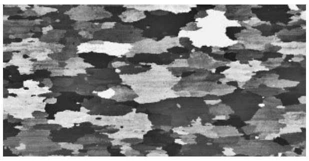
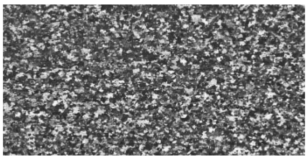
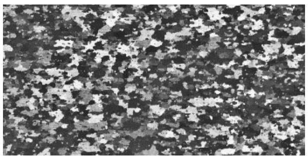
Table 2. Pre- and post-brazed ensile properties of fin stocks.

Alloy	Pre-brazed			Post-brazed		
	UTS (MPa)	0.2% YS (MPa)	EL (%)	UTS (MPa)	0.2% YS (MPa)	EL (%)
S15	167	161	2.4	102	43	8.5
S15Z	177	171	1.9	105	43	9.5
S8	188	177	4.8	125	48	7.4
S8Z	195	184	3.6	128	51	6.8

Pre-brazed tensile strength was increased with increasing Si and Zr contents in Al-Mn alloys. Post-brazed tensile strength was increased by approximately 20MPa with increasing Si addition. Meanwhile, Zr addition have a small effect on post-brazed tensile strength regardless of Si contents.

3.2 Recrystallized grain structure

Fig. 1 and 2 show pre- and post-brazed recrystallized grain structure and grain size after brazing heat treatment of fin stocks.

Alloy	Before brazing heat treatment
S15	
S15Z	
S8	
S8Z	

5mm

Fig. 1. Pre-brazed recrystallized grain structure of fin stocks.

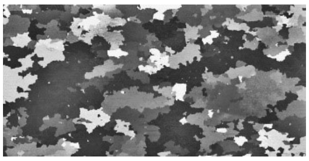
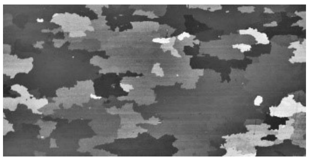
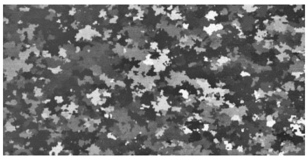
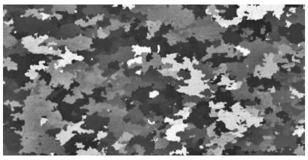
Alloy	After brazing heat treatment	Grain size (μm)
S15		1400
S15Z		2200
S8		700
S8Z		1200

Fig. 2. Post-brazed recrystallized grain structure and grain size of fin stocks.

5mm

As revealed in Fig. 1 and 2, in all fin stocks, post-brazed recrystallized grains was larger than that of pre-brazed fin stocks. Post-brazed recrystallized grain size tended to decrease with increasing Si contents. On the other hands, Zr addition led to larger post-brazed grain structures regardless of Si contents. Fig. 3 shows the softening behavior during brazing heat treatment. The hardness of all fin stocks dropped off at 580 °C.

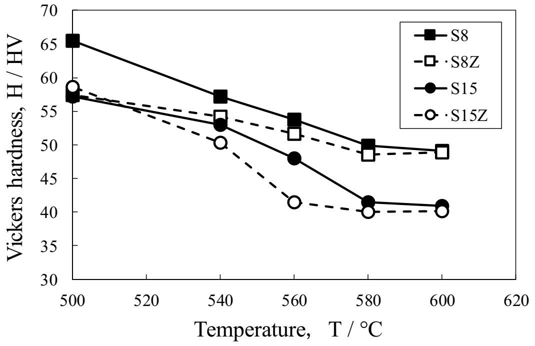


Fig.3. Softening behaviour during brazing heat treatment.

4 Discussion

4.1 Pre-and post-brazed tensile properties and microstructure

Microstructure of fin stocks were observed by SEM and TEM to investigate the effects of dispersoids distribution on tensile properties. Fig. 4 shows the distribution of secondary particles before brazing heat treatment by SEM. Based on the SEM images shown in Fig. 4, the frequency of equivalent diameters for the secondary particles was calculated using the LUZEX analysis software. Fig. 5 shows the frequency of equivalent diameters for the secondary particles in fin stocks.

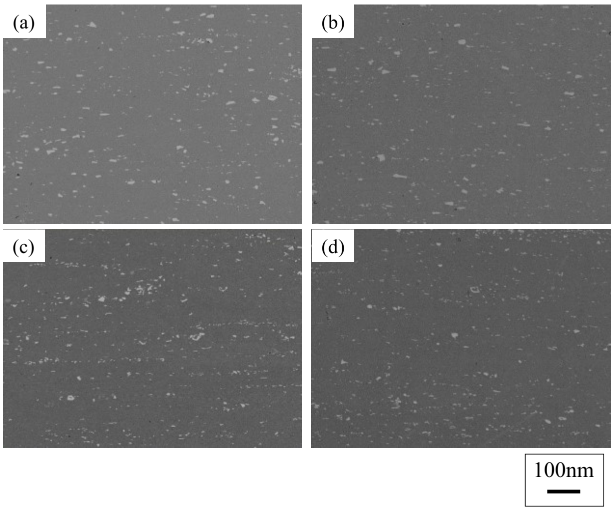


Fig. 4. Distribution of secondary particles of fin stocks before brazing heat treatment. (a)S15, (b)S15Z, (C)S8, (d)S8Z.

As shown in Fig. 5, there are no difference of distribution of secondary particles in fin stocks. It was reported that addition of Si to Al-Mn alloys have small effect on the distribution of coarse secondary particles, meanwhile, Si addition tend to increase the number of fine dispersoids [7].

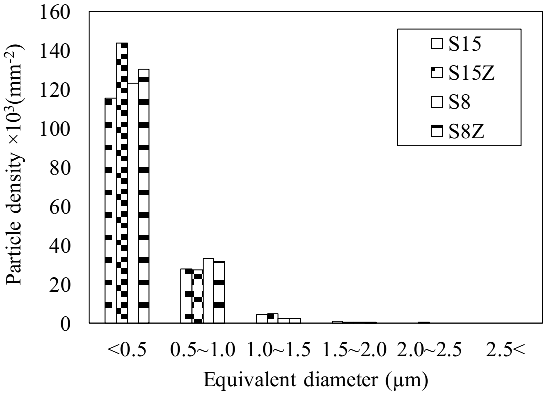


Fig. 5. Particle density of equivalent diameter for secondary particles in fin stocks.

Fig. 6 shows the TEM image of S15Z and S8Z samples before brazing heat treatment. In this study, a number of fine dispersoids were observed in S8Z sample (high Si contents). In addition, Al(Mn,Fe)Si dispersoids were detected by the TEM-EDS.

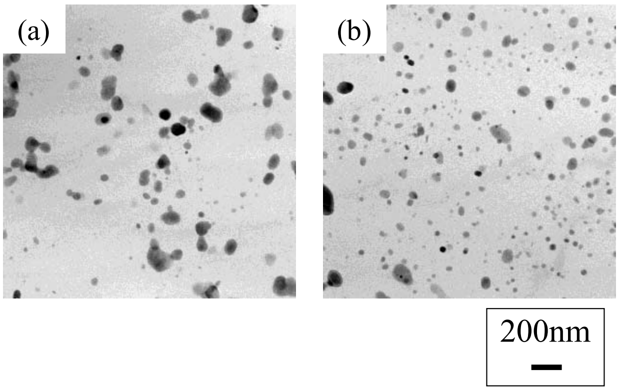


Fig. 6. Distribution of fine dispersoids of fin stocks before brazing heat treatment. (a)S15Z, (b)S8Z,

Zr-containing dispersoids were observed in S15Z and S8Z samples before brazing heat treatment (Fig.7). Fine dispersoids were observed in both samples. Regarding Zr-containing dispersoids, peaks of Al and Zr were detected in S15Z sample, but peaks of Al, Zr and Si were analysed in S8Z sample before brazing heat treatment by TEM-EDS. The EDS analysis results reveal that Si is incorporated inside dispersoids to produce (Al, Si)$_3$Zr in S8Z sample. The amounts of Mn and Zr solute in fin stocks before and after brazing heat treatment were shown in Table 3. There are less amounts of Mn and Zr solute in matrix before brazing heat treatment. On the other hands, the amounts of Mn and Zr were increased after brazing heat treatment. Fine dispersoids, such as Al$_3$Zr, (Al,Si)$_3$Zr and Al(Mn,Fe)Si, likely to be dissolved in brazing heat treatment at 600 °C. Therefore, these results suggest that the reason for the effect of Zr addition on post-brazed tensile strength was small is due to the decrease of the number of fine dispersoids during brazing heat treatment.

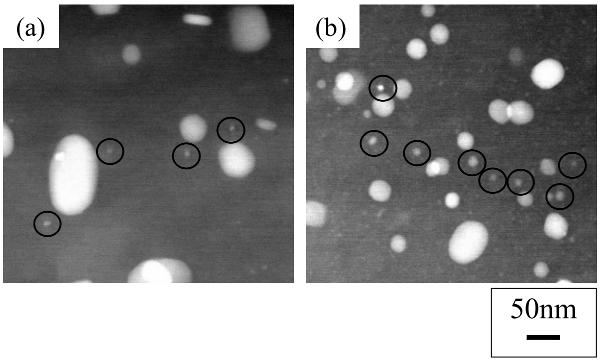


Fig. 7. Distribution of Zr-containing dispersoids in fin stocks before brazing heat treatment. (a) S15Z, (b) S8Z. Black circules indicate Zr-containing dispersoids.

Table 3. Amounts of Mn and Zr solute in matrix before and after brazing heat treatment. (mass%)

	Mn		Zr	
	Before brazing	After brazing	Before brazing	After brazing
S15	0.16	0.34	–	–
S15Z	0.13	0.30	0.02	0.04
S8	0.04	0.13	–	–
S8Z	0.04	0.12	0.03	0.04

4.2 Effects of Si and Zr on Recrystallization behavior

In previous studies, it is widely known 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) [3].

It was reported that large secondary particles (> 1 µm) act as nucleation sites of recrystallization. As shown in Fig. 4 and 5, Addition of Si and Zr to Al-Mn alloys 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.

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. As shown in Table 3, Mn and Zr solutes before brazing heat treatment were insignificant amounts. Therefore, the influence of the solute atoms on recrystallization behavior during brazing heat treatment was considered to be similar.

Fine dispersoids of less than about 100 nm affected the recrystallization behavior because they exert a drag force on the movement of subgrain boundaries. As shown in Fig.7, the size of Al_3Zr and $(Al,Si)_3Zr$ dispersoids were refiner than that of Al(Mn,Fe)Si dispeorsoids. Therefore, it was considered that Al_3Zr and $(Al,Si)_3Zr$ despersoids effectively act as pining the grain boundaries and subgrains. In this studies, chemical composition of dispersoids was changed to $(Al, Si)_3Zr$ from Al_3Zr by addition of Si. However, no change of size, distribution and a number of disersoids were observed. Thus, although addition of Zr led to larger recrystallized grain structure during brazing heat treatment, it was considered that increase of Si have a relatively small effect in continous cast Al-Mn-Zr alloy fin stocks.

4 Discussion

To the application of the continuous cast fin stocks, effects of Si and Zr addition on pre- and post-brazed tensile properties and recrystallization behaviour after brazing heat treatment of Al-Mn alloy fin stocks were studied. The main results can be summarized as follows:

1. Pre-brazed tensile strength was increased with increasing Si and Zr contents in Al-Mn alloys. It was supposed that fine Al(Mn, Fe)Si and Al_3Zr or $(Al,Si)_3Zr$ dispersoids were distributed in matrix. However, Zr addition have relatively small effect on post-brazed tensile strength regardless of Si contents. This is because fine Al_3Zr or $(Al,Si)_3Zr$ dispersoids were dissolved during brazing heat treatment.

2. Coarsely recrystallized grain structure after brazing heat treatment of Al-Mn-Si alloy fin stocks was obtained by addition of 0.1%Zr. It was considered that fine Al_3Zr and $(Al,Si)_3Zr$ were effective for Zener-drag. However, no observation of size, distribution and a number of disersoids were confirmed. Although addition of Zr led to larger recrystallized grain structure during brazing heat treatment, it was considered that increase of Si have a relatively small effect in continous cast Al-Mn-Zr alloy fin stocks.

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