Published in the Proceedings of the 16th International Aluminum Alloys Conference (ICAA16) 2018
ISBN: 978-1-926872-41-4
by the Canadian Institute of Mining, Metallurgy & Petroleum

EFFECT OF CU ADDITIONS UPON THE STRENGTHENING MECHANISMS AND RECRYSTALLIZATION BEHAVIOR IN Al-Mn-Fe-Si HEAT EXCHANGER FIN STOCK

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ABSTRACT

Previous work has shown that the strengthening Al-Mn alloys with copper leads to the formation of an undesirable reduction in recrystallized grain size. In this study the mechanisms of strengthening and recrystallization behavior in a continuously cast automotive heat exchanger fin stock of Al-1.1wt%Mn-0.5wt%Fe-0.3wt%Si with a 0.3wt%Cu addition were investigated. Metallurgical analysis revealed that the Cu strengthening was dominated by the formation of dispersoid particles, while solid solution strengthening decreased with the Cu additions. This result is attributed to the decrease in the amount of Mn solid solution. The post brazing recrystallized grain size was reduced compared to that not containing Cu. It is postulated that the Cu addition leads to a decrease in the amount of Mn in solid solution which leads to a finer grain size. This effect is attributed to Mn in the aluminum matrix inhibiting boundary migration but allowing other grains to grow during heat treatment. The results are rationalized based on particle stimulated nucleation (PSN), wherein dispersoid particles are more likely to become active recrystallization nuclei during the heat treatment. The increase in the number of active dispersoid particles with Cu addition is correlated to the recrystallized grain structure.

KEYWORDS

Heat exchanger, Fin stock, Continuous cast, Brazing, Manganese, Copper, Strength, Recrystallization

INTRODUCTION

Improvements in properties such as strength, brazeability and corrosion resistance in thermal fin stock alloys are all means to gain improved efficiency in heat exchangers particularly in automotive applications. While Al-Mn alloys dominate automotive heat exchanger fin stock alloy, even small chemical compositional changes can profoundly influence these properties (Kawahara et al., 2004; Yoshino et al., 2009). The microstructure (particularly the grain size and shape) also plays a key role in determining the product performance and hence the thermo-mechanical processing (TMP) must also be considered. The casting method (typically conventional direct chill, DC, or continuous casting) significantly influences the properties in no small part due to the very different TMP routes that are used. Continuous casting is generally favored for fin stock applications as its higher cooling rate (which can be 2 to 3 orders of magnitude higher than DC casting) leads to finer as-solidified intermetallic particles and an increase in super-saturated solid solution elements (such as Mn) that are known to improve fin stock performance such as strength, brazeability (Oki et al., 2008).

With a view of to improve Al-Mn based fin stock alloy properties, the effects of minor changes to the alloy composition have been also investigated in previous work (Kawahara et al., 2004; Yoshino et al., 2009). That work has shown that minor Cu additions in Al-Mn heat exchanger fin stock alloys can significantly influence the properties. Previous work has reported that Cu additions can increase strengthening, alters the recrystallization behavior and the corrosion properties. Cu has been found to lead to a reduction in corrosion resistance in Al-Mn alloys. This effect was shown to be the result of the formation of cathodic Cu precipitates which accelerates corrosion on the fin stock surface (Yoshino et al., 2009). The post heat treatment recrystallized grain size decreased with Cu addition, although the fine grain structure is known to negatively affect the brazeability in fin stock alloys because of erosion (Kawahara et al., 2004; Oki et al., 2008). The tensile properties show a marked increased with Cu addition, and this increase is attractive to further improve the efficiency of heat exchangers as it can lead to a gauge decrease. In this work we examine the changes of the properties in a continuously cast fin stock alloy, with Cu the metallographic mechanisms has not been clear on the strengthening and the recrystallization behavior of Cu added Al-Mn heat exchanger fin stocks. This study investigates the effect of a Cu addition on the strengthening mechanisms and recrystallization behavior in Al-Mn-Fe-Si based heat exchanger fin stock alloy produced via continuous casting.

EXPERIMENTAL PROCEDURE

The chemical compositions of the melts used in this investigation were measured via Spark Optical Emission Spectroscopy (OES/Spark) and are given in Table 1.

Table 1. Chemical composition of the alloys (weight %)

	Si	Fe	Cu	Mn	Al
0wt%Cu	0.29	0.48	<0.01	1.1	Bal.
0.3wt%Cu	0.30	0.51	0.3	1.1	Bal.

The alloys were continuously cast as thin, and were cold rolled to a final gauge of 0.10 mm. In one simulation, no hot work was used so as to better simulate an efficient continuous casting process route. In order to meet the requirement of an H16 temper, samples were also prepared using an intermediate anneal treatment for 2 hours at 450°C; which was carried out at a gauge of 0.20 mm. The 0.10 mm thickness samples were then heat treated for 3 minutes at 600°C to simulate a brazing heating cycle. The recrystallized grain structure at the surface of the 0.1 mm gauge material was observed by optical microscopy. The post braze tensile properties were also measured in a direction parallel to the rolling direction. The amount of each element in aluminum matrix was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES) after being extracted chemically in phenol. The solid solution Si was obtained by subtracting the Si amount contained in the undissolved residual from the Si amount from the initial melt chemistry. Dispersoid particle distributions were evaluated via SEM and TEM analyses.

RESULTS

Tensile Properties

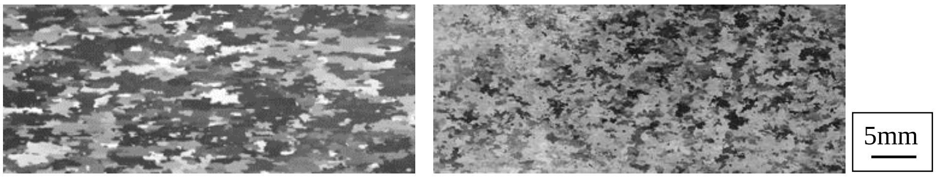
The tensile properties of the fin stocks after brazing heat treatment are shown in Table 2. Both the tensile strength and the 0.2% proof stress in 0.3wt%Cu were higher than measured in 0wt%Cu, though the elongation of the 0.3wt%Cu-containing alloy was slightly less than the Cu-free variant. This strengthening behavior is consistent with the previous work (Kawahara et al., 2004; Yoshino et al., 2009).

Table 2. Tensile properties of the fin stock materials post brazing cycle

	Tensile strength (MPa)	0.2% proof Stress (MPa)	Elongation (%)
0wt%Cu	97	42	11
0.3wt%Cu	119	45	9

Recrystallized Grain Structure

Figure 1 shows recrystallized grain structure and average grain size on the surface of the fin stocks after brazing heat treatment. The grain size of 1600 μm in 0.3wt%Cu was smaller than 4100 μm observed in the 0wt%Cu variant. The recrystallized grain size is known to be affected by the chemical composition and such a large variation in the post brazing heating cycle is typically observed in continuous cast fin stock (Kawahara et al., 2004). Both the fin stock variants in this study formed significantly larger grains than would be observed in conventionally produced DC cast fin stock, as observed in the previous work (Yoshino et al., 2016). Large grain structures, such as observed in both continuously cast variants, would be beneficial to improve the product brazeability.



0wt%Cu: 4100 μm 0.3wt%Cu: 1600 μm

Figure 1. Recrystallized grain structure and average grain size on the surface of the fin stock sheets after brazing heat treatment

DISCUSSION

Strengthening Mechanisms

Grain size, solid solution, dispersoid particles and dislocations for work hardening can be generally considered as microstructural factors for influencing strength in this alloy system. However, the work hardening was excluded from this investigation because the samples were in the fully-annealed state following the brazing heat treatment cycle performed at 600°C. Thus, the studied strengthening mechanisms are the grain size, solid solution and dispersoid strengthening. The effect of grain size on strength (yield strength is σ_G) may be calculated using the Hall-Petch relationship (Khakbaz et al., 2012):

$$\sigma_G = \sigma_0 + \frac{k_y}{\sqrt{d}} \quad (1)$$

where σ_0 and k_y are material constants and d is grain size. The calculated yield stresses are shown in Table 3. The measured yield strength of the 0.3wt%Cu fin stock was 43 MPa, and that of the 0wt%Cu was 42 MPa, which is within the normal statistical scatter of these materials properties; that is, both samples exhibited the same yield strength.

Table 3. Calculated yield strength using Hall-Petch relationship (1) including the change in the yield stress, $\Delta\sigma_G$, with 0.3wt%Cu addition (MPa)

0wt%Cu	0.3wt%Cu	$\Delta\sigma_G$
42	43	+1

In order to evaluate the solid solution strengthening, the solid solute amount of each element in the aluminum matrix was measured after the intermediate annealing and after the brazing heat treatment. Figure 2 shows the amount of solid solution Mn in the 0wt%Cu and 0.3wt%Cu variants.

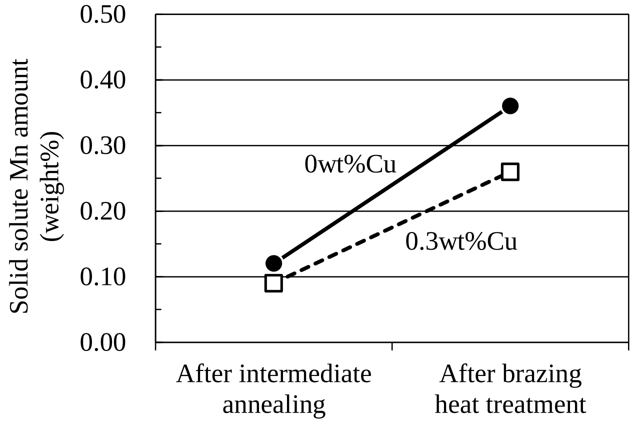


Figure 2. Amount of Mn in solid solution after intermediate annealing and after brazing heat treatment

The amount of Mn in solid solution after the intermediate annealing was estimated to be the same as in the H16 condition since the fin stock before the brazing heat treatment was only cold rolled after the intermediate anneal. The amount of Mn in solid solution in both 0wt%Cu and 0.3wt%Cu after the intermediate annealing were about 0.1wt%Mn. After the brazing heat treatment, the amount of Mn in solid solution in both 0wt%Cu and 0.3wt%Cu increased. However, the solid solute Mn in the 0.3wt%Cu variant was found to be 0.1wt% smaller than that in 0wt%Cu. The changes in the amount of solid solution Si, Fe and Cu amounts with brazing heat treatment were smaller than the change in solid solute Mn amount. With regard to solid solution strengthening about each element, the increase in yield stress $\Delta\sigma_S$ is calculated using the following equation (Higashi, 2010):

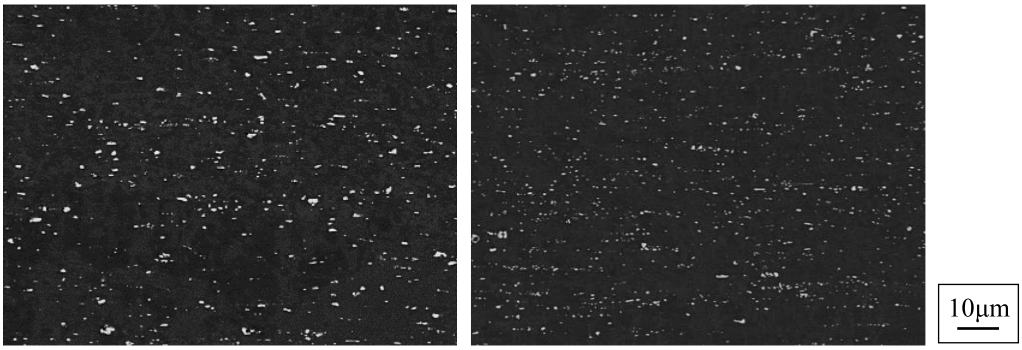
$$\Delta\sigma_S = \frac{3^{3/4}}{2}\left(\frac{1+\nu}{1-\nu}\right)^{3/2} M\mu|\varepsilon|^{3/2}\sqrt{c} \qquad (2)$$

where ν is Poisson's ratio, M is Taylor factor, μ is rigidity, ε is misfit strain by each element and c is solid solute amount of each element. The calculated changes in yield stress by solid solution strengthening with 0.3wt%Cu addition are given in Table 4. The decrease in the yield stress accompanied by the decrease in solid solute Mn was noticeable with 0.3wt%Cu addition, even though the increases in the yield stress by solid solution Fe and Cu were calculated. The change in the yield stress by solid solution strengthening in the sample with the 0.3wt%Cu addition resulted in an overall decrease of 6 MPa. The decrease in solid solution Mn strengthening is believed to have caused the degradation of total yield stress with 0.3wt%Cu addition.

Table 4. Changes in the yield stress by solid solution strengthening $\boldsymbol{\Delta\sigma_s}$, with 0.3wt%Cu addition (MPa)

Si	Fe	Cu	Mn	Total $\boldsymbol{\Delta\sigma_s}$
–1	+3	+3	–11	–6

According to Orowan mechanism, strengthening is attributed to dispersoid particles distributed in aluminum matrix, and the Orowan strengthening is further influenced by the dispersoid particles distribution. Using back scatter imaging SEM, the distribution of dispersoid particles on the cross sections of fin stocks after brazing heat treatment are shown in Figure 3.



0wt%Cu 0.3wt%Cu

Figure 3. Dispersoid particles distribution in 0wt%Cu and 0.3wt%Cu after brazing heat treatment

0wt%Cu and 0.3wt%Cu differed in the distribution of dispersoid particles. The particle size of 0.3wt%Cu was smaller than that of 0wt%Cu, but the number of the particles in 0.3wt%Cu was more than that in 0wt%Cu even though those particles uniformly were distributed in both 0wt%Cu and 0.3wt%Cu. The Orowan strength, τ_{OR}, may be calculated using the following equation (Orowan, 1948):

$$\tau_{OR} = \frac{\mu b}{L_0} \tag{3}$$

with μ being rigidity, b Burgers vector and L_0 average interval of dispersoid particles. Each average intervals, L_0, in 0wt%Cu and 0.3wt%Cu was calculated using the number of dispersoid particles per unit area (Noguchi et al., 1984). The Taylor factor, M, may be subsequently used to convert the Orowan stress, τ_{OR}, into yield strength, σ_{OR}, using the following equation:

$$\sigma_{OR} = M * \tau_{OR} \tag{4}$$

and the yield strength, σ_{OR}, was then calculated and the results are shown in Table 5.

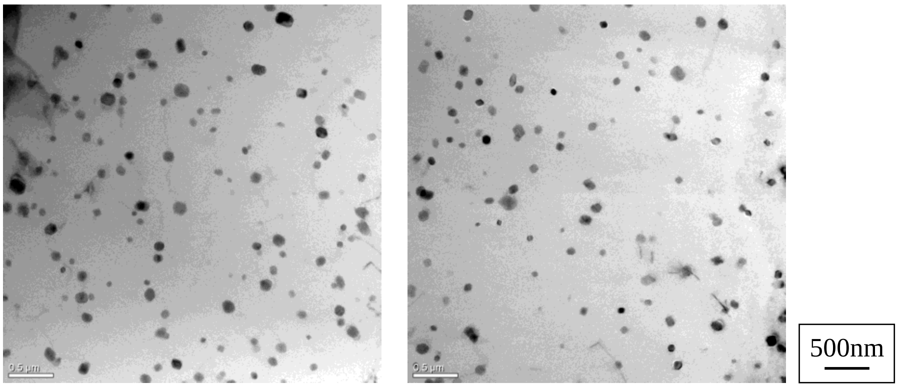
Table 5. Yield stresses calculated from Orowan strength and the change in the yield strength, $\Delta\sigma_{OR}$, with 0.3wt%Cu addition (MPa)

0wt%Cu	0.3wt%Cu	$\Delta\sigma_{OR}$
19	26	+7

By summing together the individual yield strength components, $\Delta\sigma_G$, $\Delta\sigma_S$ and $\Delta\sigma_{OR}$, and the change in total yield stress $\Delta\sigma_Y$ may be calculated. $\Delta\sigma_Y$ was estimated as 2 MPa increasing with the 0.3wt%Cu addition. As shown in Table 2, the actual increase in the yield stress with 0.3wt%Cu addition was measured at 3 MPa, which shows reasonable correlation with the as-calculated values. However, as each constituent may contribute to the overall $\Delta\sigma_G$, $\Delta\sigma_S$ and $\Delta\sigma_{OR}$ values, it should be noted that the dispersion strengthening effect contributes most strongly to the overall change in the yield strength, while concomitantly the decrease of Mn in solid solution prevented the fin stock from significantly improving the strength. The recrystallized grain size had a small impact on the yield strength in the continuous cast fin stock of this study.

Recrystallization Behavior

As shown in Figure 1, the 0.3wt%Cu addition resulted in a smaller recrystallized grain size after the brazing heat treatment than observed in the 0wt%Cu variant, even though both have relatively coarse grain structure. Previous studies (Nes et al., 1975; Nes, 1976; Engler et al., 1996) have shown that Mn particles and solid solute Mn in the aluminum matrix affect the recrystallization behavior after heat treatment. Fine precipitates and Mn in solid solution lead to large recrystallized grains as they are of the correct size to act as obstacles to dislocation migration during heat treatment; even though relatively coarse dispersoids including constituent particles can promote the formation of fine recrystallized grains after heat treatment. Figure 4 shows the distribution of fine precipitates observed in TEM about the fin stocks after brazing heat treatment.



0wt%Cu 0.3wt%Cu

Figure 4. Distribution of fine precipitates in 0wt%Cu and 0.3wt%Cu after brazing heat treatment

The fine precipitates in 0.3wt%Cu have a very similar distribution as observed in 0wt%Cu. This suggests that the influence of the precipitates on the recrystallization behavior would be identical. In Figure 2 we noted the lower amount of Mn in solution in the 0.3wt%Cu variant than observed in 0wt%Cu after the brazing heat treatment. The smaller recrystallized grain structure of 0.3wt%Cu than that of 0wt%Cu, as shown in Figure 1, is due to less Mn in solid solution in 0.3wt%Cu leading to a coarser recrystallized grain structure. Furthermore, as shown in Figure 3, with regard to recrystallization nucleation, 0.3wt%Cu clearly showed a greater number of dispersoids, which would act as nuclei sites for recrystallization compared to the in 0wt%Cu. As found in the previous study (Engler et al., 1996), particle stimulated nucleation (PSN) during recrystallization is caused by dispersoid particles in Al-Mn alloy. Consequently, it can be stated that the higher number density of dispersoids in the 0.3wt%Cu could increase the nucleation rate, resulting in a finer recrystallized grain structure.

CONCLUSIONS

In this work, the effect of a Cu addition on the strengthening mechanism and recrystallization behavior was investigated in a continuous cast Al-Mn-Fe-Si heat exchanger fin stock alloy. The following has been found.

A 0.3wt%Cu addition to a continuous cast fin stock alloy enhanced the strengthening after a brazing heat treatment. With regard to the strengthening mechanism, it appeared that dispersion strengthening mainly contributed to the increase in yield stress. The overall solid solution strengthening component decreased with the 0.3wt%Cu addition which was attributed to a reduction in the level of Mn solute in the 0.3wt%Cu alloy. The effect of grain size on the yield stress in 0.3wt%Cu was almost equivalent to that in 0wt%Cu.

The smaller recrystallized grain structure in 0.3wt%Cu alloy, after a brazing heat treatment, is again attributed to less solute Mn, as well as an increase in the number of dispersion particles. Assuming an equivalent distribution of the fine precipitates in the 0wt%Cu and 0.3wt%Cu, the effect on recrystallization would be equivalent

REFERENCES

Engler, O., Yang, P., & Kong, X.W. (1996). On the formation of recrystallization textures in binary Al-1.3% Mn investigated by means of local texture analysis. *Acta Materialia*, *44*, 3349–3369.

Higashi, K. (2010). New innovations in alchemy dreamed by the first principle—the latter part—. *Journal of Japan Institute of Light Metals*, *60*, 458–466.

Khakbaz, F., & Kazeminezhad, M. (2012). Work hardening and mechanical properties of severely deformed AA3003 by constrained groove pressing. *Journal of Manufacturing Processes*, *14*, 20–25.

Kawahara, A., Niikura, A., & Doko, T. (2004). Properties of Al-1.7Fe-1.6Mn alloy fin stock manufactured by continuous casting method, The 106th Conference of Japan Institute of Light Metals, 71–72.

Nes, E., & Embury, J. D. (1975). The influence of a fine particle dispersion on the recrystallization behaviour of a two phase aluminum alloy. *Z. Metallkd.*, *66*, 589–593.

Nes, E. (1976). The concept of a “grain size diagram” in the analysis of the recrystallization behaviour of AlMn alloys. *Aluminium*, *52*, 560–563.

Noguchi, T., Miyagi, K., Narita, T., & Nagaoka, K. (1984). The three-dimensional distribution of graphite nodules in spheroidal graphite cast iron. *The Journal of the Japan Foundrymen's Society*, *56*, 683–689.

Oki, Y., Anami, T., Okamoto, I., & Shinoda, T. (2008). Effect of intermetallic particles on high heat conductivity Al-Fe brazing fin alloy. *The 115th Conference of Japan Institute of Light Metals*, 355–356.

Orowan, E. (1948). in Symposium on Internal Stress in Metals and Alloys, London, The Institute of Metals, 451.

Yoshino, M., Edo, M., Kuroda, S., Asano, M., & Tohma, K. (2009). Effect of additional Si and Cu on strength and corrosion resistance of sacrificial anode fin stock for automotive heat exchangers. *Journal of Japan Institute of Light Metals*, *5*9, 229–235.

Yoshino, M., Iwao, S., Edo, M., Muraishi, S., & Kumai, S. (2016). Effects of homogenization and brazing conditions on material properties of brazed Al-Mn base alloys. *Journal of the Japan Institute of Light Metals*, *66*, 652–659.