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

CONTROL OF RECRYSTALLIZATION IN COLD-ROLLED AlMn(Mg)ScZr SHEET FOR BRAZING APPLICATIONS

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ABSTRACT

The occurrence of recrystallization in cold-worked aluminum sheet during the brazing process leads to loss of strength, an inhomogeneous grain structure and reduced corrosion resistance. AlMgScZr alloys are known for their extraordinary recrystallization resistance due to the influence of Sc and Zr addition on their microstructure. Here, we investigate the effect of alloy composition (i.e. Mn, Mg, Sc, Zr content), cold-roll reduction and pre-aging treatment on the recrystallization behavior of cold-rolled sheets at brazing temperatures typically used during the manufacture of heat exchanger units. The analysis of recrystallization behavior is carried out through microstructural characterization and the results are compared with the behavior of a commercial, AA3xxx-based heat exchanger alloy.

KEYWORDS

Recrystallization, Precipitation, Aluminum-scandium alloys, Microstructure characterization, Brazing

INTRODUCTION

Control of recrystallization is of critical importance during brazing, which is a widely-used joining technique for aluminum alloys in aircraft structures (Heinz, 2000) and automotive heat exchangers (Miller, 2000; Marshall, 1993). Due to excessive local heat at brazing temperatures, the cold work texture of aluminum alloys in the cold-rolled sheets may undergo a local recrystallization process (Marshall, 1993). This leads to the formation of an inhomogeneous microstructure and thus anisotropic mechanical properties (Miller, 2000) and low corrosion resistance (Marshall, 1993) across the sheet. X800, a commonly-used Al-Mn alloy series for automotive heat exchangers applications, has been developed specifically for a higher strength as well as an enhanced corrosion resistance as opposed to the traditionally-used AA3003 alloy (Marshall, 1993). X800 alloys, however, exhibit a low recrystallization resistance at normal brazing temperatures, i.e. 590°C. In contrast, Al-Sc-Zr alloys have been shown to exhibit an extraordinary recrystallization resistance at such temperatures (Riddle, 2004) while also being corrosion resistant and possessing a high room-temperature strength (Fuller, 2002). This has been shown to be due to the formation of coherent, nanoscale $Al_3(ScZr)$ precipitates that effectively impede grain boundaries while also exhibiting very slow coarsening kinetics at high temperatures (Riddle, 2004; Jones, 2003; Ocenasek, 2001). In this study, we analyze the recrystallization behavior of X800 alloys under brazing conditions through introducing Sc and Zr into the system as well as varying the Mn and Mg content. The effect of processing route is also studied by introducing a pre-aging stabilization treatment as well as varying the cold-roll reduction prior to the final brazing anneal.

EXPERIMENTAL PROCEDURE

The alloys, with the chemical composition listed in Table 1 (with values in wt% throughout the manuscript), were cast at Alcereco Inc. (Kingston ON) in the form of 10 mm-thick book molds. The as-cast ingots were cold-rolled down to 2.5 mm and 0.5 mm gauges (called CR2.5 and CR0.5, respectively, hereafter). Half of the cold-rolled sheets underwent a pre-aging stabilizing treatment at 450°C followed by an isothermal annealing treatment at 590°C (called CR2.5-Ag450-An590 and CR0.5-Ag450-An590, hereafter). The other half were directly annealed at 590°C (called CR2.5-An590 and CR0.5-An590, hereafter). The pre-aging treatment, in this study, was performed at 450°C for 4 hours with heating and cooling ramps of 50°C/hr. Such pre-aging temperature and procedure have been utilized in ref. (Riddle, 2004) in order to stabilize the evolution of $Al_3(Sc,Zr)$ precipitates in the microstructure of AlMgScZr alloys to minimize recrystallization during the subsequent hot rolling. The final annealing treatment was performed isothermally for 0.5 hours at 590°C which is within the typical brazing temperature range for aluminum alloys in automotive heat exchanger applications. Also, the brazing heat cycle to 590°C normally takes about half an hour.

The evolution of microstructure and phases at various conditions were studied using Optical Microscopy and Scanning Electron Microscopy (SEM). For optical microscopy, specimens were cut from the longitudinal cross-section of the rolled/heat-treated sheet. The specimens were mounted in Bakelite and then mechanically ground using SiC grinding papers, followed by fine polishing with diamond suspensions and then finished with colloidal silica. The polished specimens were etched with Barker's etch at 30V. SEM was performed using a JEOL microscope (JSM-5800) operated at 20 keV and 10 mm working distance. Energy Dispersive Spectroscopy (EDS) was performed using an Oxford Instruments INCA system.

Table 1. Chemical composition of alloys being studied (values in wt%)

Alloy	Sc	Mg	Mn	Zr	Cu
B	0	0.14	1.42	0	0.65
A1	0.2	0.14	1.5	0.12	0
A2	0.1	0.14	1.5	0.12	0
A3	0.2	0.15	0.77	0.12	0
A4	0.2	0	1.54	0.12	0

RESULTS

Figure 1 shows the microstructures revealed by Barker's Etch for various alloys and conditions. The evolution of anodized grains upon etching in Barker's solution can be used to determine whether recrystallization has occurred or the original cold-rolled grain structure has remained intact (Riddle, 2004). To highlight the criterion used to determine the recrystallization status of the microstructures shown in Figure 1, examples of unrecrystallized, partially recrystallized and fully recrystallized microstructures are presented in Figure 2. In an "Unrecrystallized" microstructure, the fibrous grains originated during the previous cold-roll remain unchanged upon the subsequent heat treatments (Figure 2(a)). A "Fully Recrystallized" microstructure, as shown in Figure 2(c), exhibits a network of recrystallized grains stretched along the original cold-roll texture. A "Partially Recrystallized" microstructure exhibits a combination of a fibrous cold-worked grain structure and elongated recrystallized grains. The recrystallized grains in Al-Sc system tend to form an elongated texture along the previous cold-worked texture orientation (Riddle, 2004; Fuller, 2002; Ocenasek, 2001), based on a phenomenon called "Extensive Recovery" or "Continuous Recrystallization" (Riddle, 2004). Using such a criterion, the recrystallization status of various alloys and conditions is summarized in Table 2.

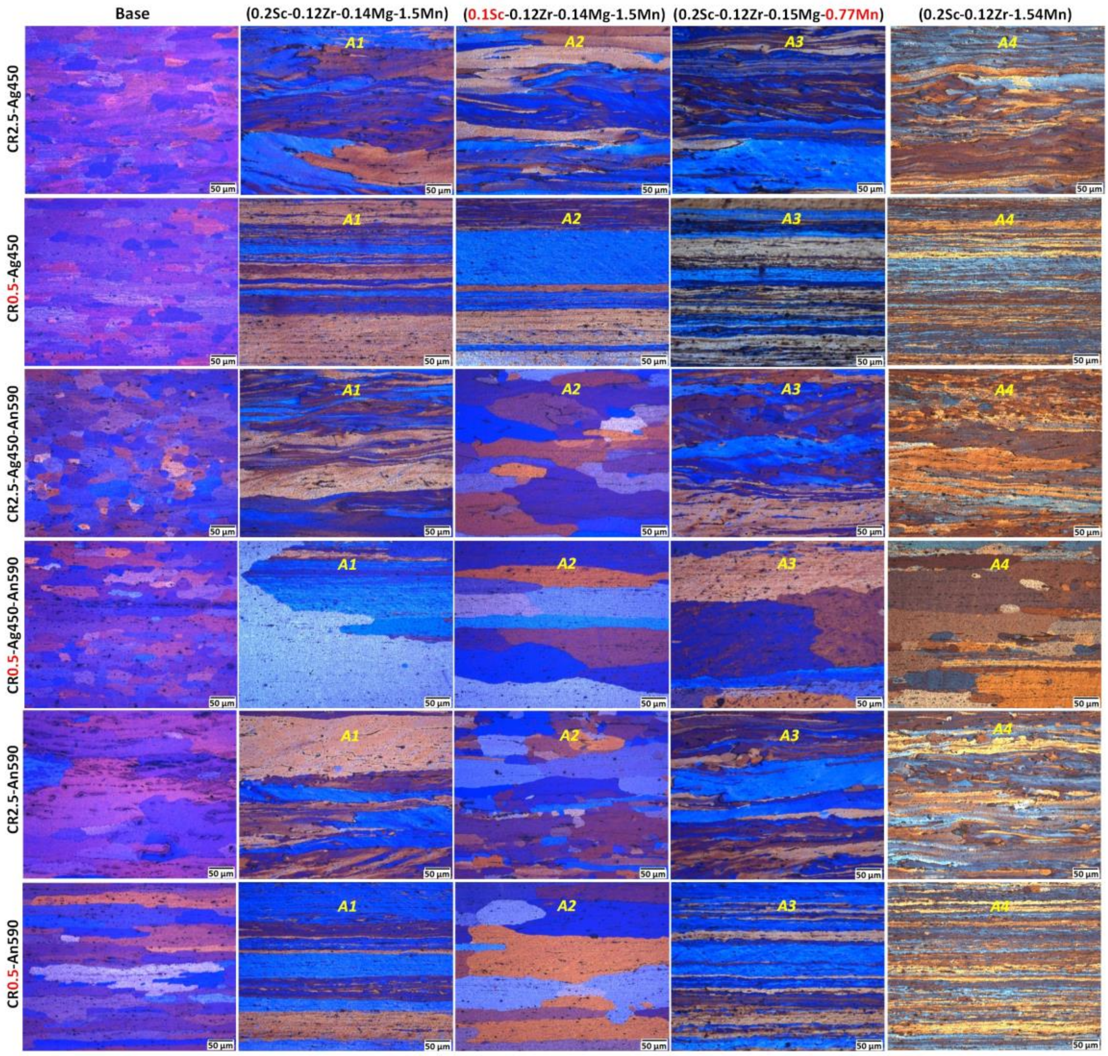

Figure 1. Optical micrographs of microstructures revealed by Barker's Etch for various alloys under different processing conditions; the matrix of images is cross-labeled by alloy composition from the top row and the processing condition from the left column.

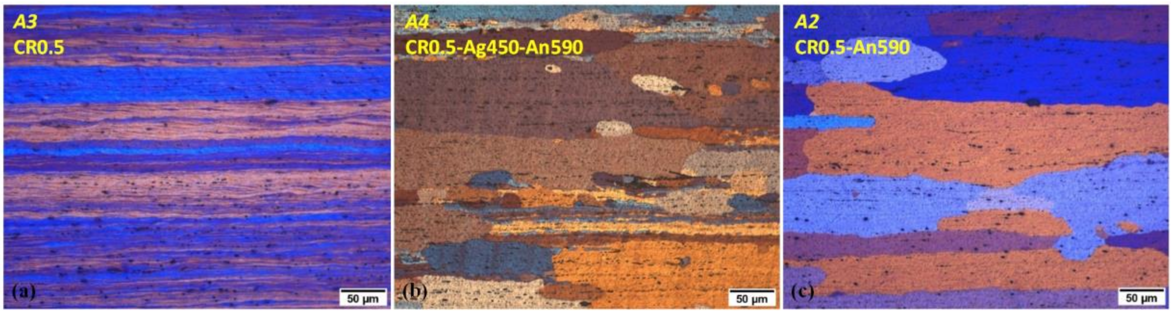

Figure 2. Optical micrographs showing examples of (a) Unrecrystallized/Cold-rolled, (b) Partially Recrystallized and (c) Fully Recrystallized microstructures in as revealed by Barker's Etch.

Table 2. Recrystallization status for various alloys and conditions

Alloy	**Cold-roll gauge (mm)**	**Recrystallization status at different tempers**		
		CR-Ag450	**CR-Ag450-An590**	**CR-An590**
B	2.5	Full	Full	Full
	0.5	Full	Full	Full
A1 (0.2Sc-0.12Zr-0.14Mg-1.5Mn)	2.5	***None***	***None***	***None***
	0.5	***None***	Partial	***None***
A2 (0.1Sc-0.12Zr-0.14Mg-1.5Mn)	2.5	***None***	Full	Full
	0.5	***None***	Full	Full
A3 (0.2Sc-0.12Zr-0.15Mg-0.77Mn)	2.5	***None***	***None***	***None***
	0.5	***None***	Partial	***None***
A4 (0.2Sc-0.123Zr-1.54Mn)	2.5	***None***	***None***	***None***
	0.5	***None***	Partial	***None***

Following the data listed in Table 2, the effect of alloy composition, pre-aging and cold-rolling reduction on recrystallization behavior can be summarized as below.

Effect of Alloy Composition

The role of Sc is critical. At 0% Sc (base alloy, *B*), full recrystallization occurs at all process conditions. At 0.1% Sc (*A2* alloy), recrystallization is prevented at the pre-aged state, but occurs at the annealed state (with or without the pre-age). At 0.2% Sc, recrystallization is prohibited for all 2.5 mm-thick sheets at the annealed state (with or without pre-age) and for 0.5 mm-thick samples at the directly-annealed state only. The Mn and Mg content (within the range examined in this study) has no visible effect on the recrystallization behavior of various alloys and conditions.

Effect of Cold-Roll Reduction

The cold-rolling reduction determines the amount of cold-work introduced to the metal and thus the stored energy; which has a critical impact on the recrystallization behavior during the subsequent anneal. Increasing the cold-rolling reduction enhances recrystallization upon subsequent annealing. At 2.5 mm thickness, alloys containing 0.2 Sc (*A1*, *A3* & *A4*) do not recrystallize in the annealed state (with or without pre-age), whereas, at 0.5 mm thickness, recrystallization is inhibited only at the directly-annealed state and for alloys containing at least 0.2Sc (*A1*, *A3* & *A4*).

Effect of Pre-Aging

Pre-aging at 450°C promotes recrystallization upon subsequent annealing of all 0.5 mm-thick samples. However, it does not affect the 2.5 mm-thick samples. Pre-aging at lower temperatures was not explored in this work and will be considered in the future studies.

Phase Analysis

To further analyze the recrystallization behavior, the evolution of phases was characterized using the SEM observations for select sheet samples at 0.5 mm thickness, with emphasis on the effect of pre-aging in Figure 3 and the effect of Sc content in Figure 4. As shown in Figure 3(a), the cold-rolled microstructure reveals a random distribution of large particles including broken-down (Mn,Fe)-rich intermetallics as well as large Mn-rich dispersoids. The former forms originally during solidification in the form of inter-dendritic phases that are rich in both Fe and Mn. The latter forms in the solid state during cooling from solidification temperatures. Both phases get crushed during the subsequent cold-rolling, appearing in the microstructure with relatively sharp edges. Figure 3(b) shows that pre-aging at 450°C populates the microstructure with Mn-rich precipitates, which also possess a Sc content slightly higher than the matrix (as determined by several point-EDX spectrums). During the subsequent anneal, a large portion of smaller precipitates dissolve back into solid solution lowering the population of Mn-rich precipitates (as can be inferred from the microstructures shown in Figure 3(d) vs. Figure 3(b)). In contrast, the microstructure of a directly-annealed sample (Figure 3(c)) reveals a bimodal matrix of very large phases (consisting of originally as-cast intermetallics and dispersoids coarsened and rounded upon annealing), as well as newly-formed dispersoids formed upon annealing. Moreover, in the directly-annealed state, the alloys with higher Sc or Mn content (*A1* vs. *A2* or *A1* vs. *A3*, respectively) exhibit a higher population of Mn-rich dispersoids, as can be inferred from the microstructures shown in Figure 4(a) vs. Figure 4(b) and Figure 4(c), respectively.

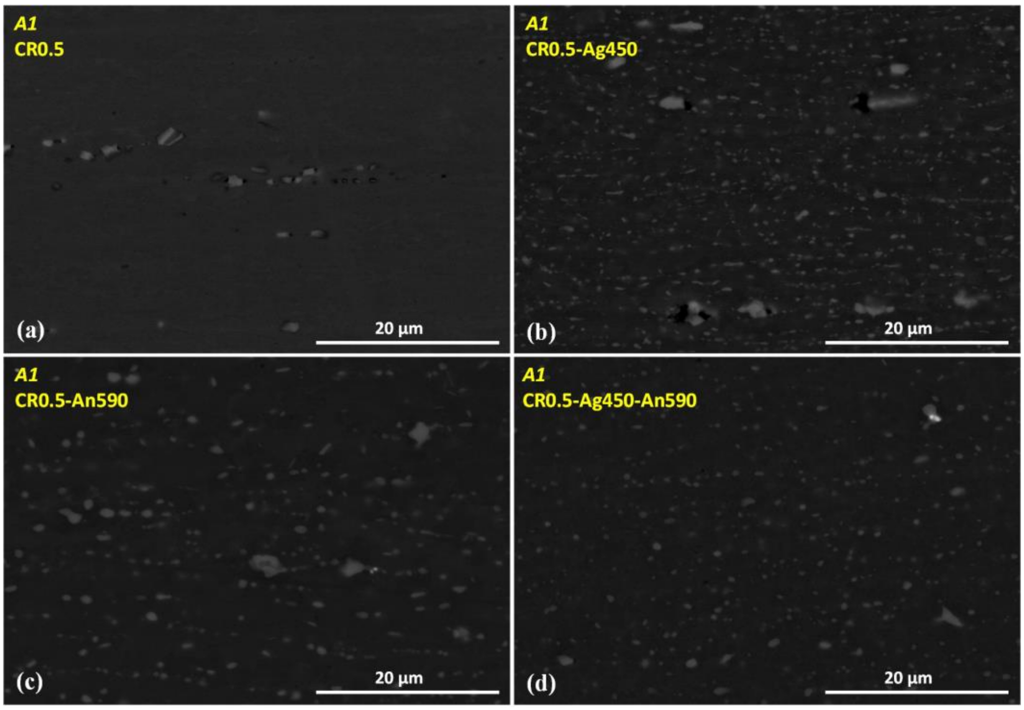

Figure 3. Backscatter SEM micrographs showing the evolution of intermetallics and dispersoids in 0.5 mm-thick *A1* (Al-0.2Sc-0.12Zr-0.14Mg-1.5Mn) sheets in (a) Cold-rolled, (b) Pre-aged, (c) Directly-annealed and (d) Pre-aged + Annealed states.

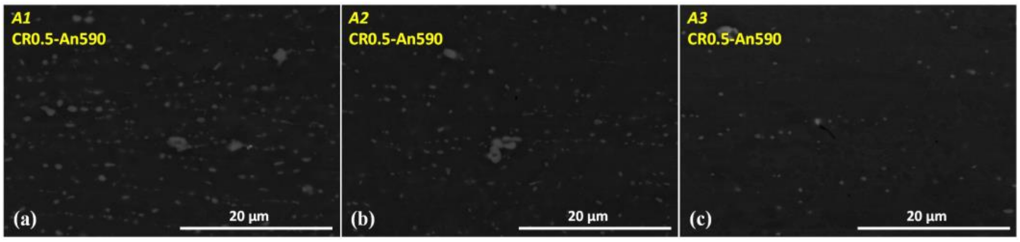

Figure 4. Backscatter SEM micrographs of intermetallics/dispersoids evolution in 0.5 mm-thick sheets of (a) *A1* (Al-0.2Sc-0.12Zr-0.14Mg-1.5Mn), (b) *A2* (Al-0.1Sc-0.12Zr-0.14Mg-1.5Mn) and (c) *A3* (Al-0.2Sc-0.12Zr-0.14Mg-0.77Mn) alloys in directly-annealed state.

DISCUSSION

Two types of phases have been identified by the SEM observations of the microstructure in samples *A1* to *A4*: (1) intermetallic phases that are rich in both Fe and Mn and (2) dispersoids/precipitates that are mainly rich in Mn. Both phases also possess slightly higher Sc content than that in the matrix. There is also a third phase, Sc,Zr-rich precipitates Al_3(Sc,Zr), that (similarly to Mn-rich precipitates) form during cooling from solidification temperatures as well as during pre-aging treatment and annealing (Fallah, 2017). However, Al_3(Sc,Zr) precipitates evolve coherently within the matrix from a few nanometers in size and, to a large extent, are resistant to coarsening even at annealing temperatures (Riddle, 2004; Fuller, 2002; Jones, 2003; Fallah, 2017; Yang, 2013). Therefore, they are normally invisible via SEM.

Al_3(Sc,Zr) precipitates are known to inhibit the grain boundary movement and thus to reduce the recrystallization kinetics during aging/annealing of AlScZr alloys (Riddle, 2004; Jones, 2003; Ocenasek, 2001; Yang, 2013). The Sc content controls the number density and size evolution of Al_3(Sc,Zr) precipitates (Riddle, 2004; Jones, 2003) and thus plays a key role in controlling the recrystallization behavior of these alloys (Riddle, 2004; Jones, 2003; Ocenasek, 2001). The higher Sc content also significantly increases the population of Mn-rich precipitates/dispersoids at the directly-annealed state, as can be seen in Figure 4(a) vs. Figure 4(b). This explains why, in the low-Sc alloy (0.1%Sc as in *A2*), full recrystallization occurs at all conditions while, under specific conditions, it can be inhibited for the high-Sc alloys (0.2%Sc as in *A1*, *A3*, *A4*), referring to Table 2. Transmission Electron Microscopy (TEM) observations will be used in an upcoming study to reveal the evolution of Al_3(Sc,Zr) precipitates and thus carry out an in-depth analysis of precipitation-recrystallization dynamics.

A higher Mn content in the alloy increases the population of Mn-rich precipitates/dispersoids (*A1* vs. *A3* in Figure 4). However, it does not seem to have a noticeable effect on the recrystallization behavior (referring to Table 2). This indicates that Mn-rich precipitates/dispersoids are not as effective as Al_3(Sc,Zr) precipitates in impeding recrystallization.

The purpose of pre-aging treatment is to stabilize the microstructure prior to annealing (brazing) treatments. As the result of pre-aging at an intermediate temperature (i.e. 450°C), a fine and uniform network of Al_3(Sc,Zr) precipitates develops in the microstructure which will inhibit the grain boundary movement during the subsequent annealing treatment at higher temperatures (i.e. 590°C). In contrast, upon direct annealing (without pre-aging) precipitation occurs concurrently with recrystallization, in which case, their competitive kinetics will control the degree of recrystallization. Moreover, at annealing temperatures, coarsening kinetics are significantly higher and precipitates quickly evolve into large dispersoids with a lower population density. The pre-aging treatment helps to stabilize the precipitate evolution and reduce the coarsening kinetics upon subsequent annealing. The selection of pre-aging temperature is, however, critical. Too high a pre-aging temperature may produce very large precipitates that have little to no effect on recrystallization. This seems to be the case for the pre-aging temperature chosen for this study, 450°C. Referring to Table 2, pre-aging has an adverse effect on resistance to recrystallization for all 0.5 mm-thick sheets, as opposed to direct annealing. This may point to a too high temperature for pre-aging treatment leading to the formation of a network of ineffective, large precipitates, that are even less effective than those developed via direct-annealing. Also, the SEM micrograph in Figure 3(b) shows that, due to pre-aging, a large number density of coarse Mn-rich precipitates/dispersoids form in the microstructure. These precipitates, which also carry an Sc content higher than the surrounding matrix, cause a depletion in the amount of Sc in the solid-solution. This potentially reduces the precipitation kinetics of Al_3Sc precipitates that form concurrently and during the subsequent anneal. To better resolve the mechanisms controlling the precipitation-recrystallization behavior, in a future study, lower pre-aging temperatures will be examined as well as TEM observations of precipitate evolution.

The cold-roll reduction also has a critical impact on the recrystallization behavior, since it controls the amount of stored energy in the sheet prior to pre-aging and/or annealing. Referring to Table 2, all 2.5 mm-thick sheet (except for the base alloy, *B*, and the low-Sc alloy, *A2*) are resistant to recrystallization under all conditions, while 0.5 mm-thick sheets of the same alloys are recrystallization-resistant only in the directly-annealed state.

SUMMARY

In this study, our experimental findings identify the critical role of alloy composition and thermomechanical processing route in the recrystallization behavior of AlMn(Mg)ScZr alloys at normal brazing temperatures (~600°C). The Sc content in the alloy is the most critical factor where a minimum of 0.2% is needed to prevent recrystallization regardless of thermomechanical processing route taken. This points to a high dependency of recrystallization resistance on the population of $Al_3(Sc,Zr)$ precipitates which is a strong function of Sc content in the alloy. The cold-roll reduction, and thus the amount of restored energy in the sheets prior to brazing, is also significantly influencing the recrystallization behavior; i.e. 2.5 mm-thick sheets are much more resistant to recrystallization than 0.5 mm-thick sheets. Pre-aging stabilizing treatment at 450°C has an adverse effect on the recrystallization resistance. We speculate that a pre-aging temperature of 450°C may have created a scarce network of large precipitates that are ineffective agents for grain boundary impingement during the subsequent anneal at the brazing temperature. In an upcoming study, the pre-aging temperature will be optimized through an in-depth TEM analysis of precipitates evolution.

ACKNOWLEDGMENTS

The authors would like to acknowledge Scandium International for supporting this investigation, Mr. R. Lees and Mr. E. Luce of Alcereco Inc. for the casting and fabrication of the materials and Dr. D. J. Lloyd for his many useful discussions.

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