

Development of Al-Mn-Cu-Mg Brazing Sheet Core Alloys for Automotive Heat Exchanger Units for Service at High Temperatures

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ABSTRACT

New aluminum alloys, based on a commercial Al-Mn-Cu brazing sheet core alloy, with increasing alloying element Mg up to 2 wt.%, have been developed for automotive heat exchanger units in service at above 200°C. The new Al-Mn-Cu-Mg alloys are to be used as the core material in brazing sheets for vacuum and nickel brazing technologies. They were DC cast to 3.75" lab sized ingots, scalped, re-heated to 520°C, hot rolled to 4.8 - 5mm, and cold rolled down to a final gauge of 1mm. It has been demonstrated by various mechanical and corrosion testing that Mg contributes a strong solid solution hardening effect at both the room and elevated temperatures, without damaging the other mechanical properties or corrosion resistance. Hence the alloys with 1 - 2 wt.% Mg are able to maintain high yield strength above 60 MPa at 200 - 300°C, with no reduction in formability and very limited decrease in corrosion resistance. Since the new alloys do not contain expensive alloying elements, there is no significant increase in material or processing costs.

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INTRODUCTION

Aluminum brazing sheet alloys have been used to make automotive heat exchanger units since 1970s. An aluminum brazing sheet is a sandwich-like composite made up of a core alloy and one or more clad alloy(s). In most high quality long life brazing sheet products, the core alloys are AA3xxx Al-Mn-Cu system which provides strength and corrosion resistance, while the clad alloys are AA4xxx Al-Si system with 7 - 12 wt.% Si, providing a low melting point filler material for brazing [1,2]. The clad is bonded to the core by roll-bonding during hot rolling or by co-casting during ingot casting [3,4]. After roll-bonding or co-casting, the brazing sheet is rolled to the desired gauge, slit to width, shipped to customer, formed and assembled into heat exchanger units, then gone through a brazing process. In a typical brazing cycle, the heat exchanger unit is heated to approximately 600°C, where the Al-Si cladding with low melting temperature begins to melt and joins the fin-and-tube assembly together, which is the main part of a heat exchanger unit [5,6]. There are many brazing technologies, but currently in industry the three major ones are the flux brazing, nickel brazing, and vacuum brazing [7,8].

The core alloys of aluminum brazing sheets are the most critical in automotive heat exchanger applications. They must maintain the desired strength and corrosion resistance at service temperature, which is well above the room temperature. Otherwise, catastrophic failure such as leaking may happen. Most of the commercial core alloys were initially designed for service temperatures below 150°C and the compositions were modified from either AA3003 or AA3005. The post-brazing yield strength (YS) of these commercial sheets is typically between 35 and 65 MPa at the room temperature, and it

usually has only limited reduction when in service at temperatures below 150°C. However, the strength drops rapidly at higher temperatures, especially above 200°C. This is particularly important because most heat exchangers for light duty applications are made of relatively thin brazing sheets. The service temperature of automotive exchanger units depends on many factors, such as engine RPM, displacement and pressure but most importantly on application. Although it is usually below 150°C for lubrication and power transfer systems for engine, transmission and occasionally hydraulics, supercharger and turbocharger technologies are limited more by the maximum allowable service temperature of the aluminum charge air coolers. In fact, if these heat exchangers could endure higher operating temperatures, increased boost and therefore increased fuel economy could be achieved. As charging technologies become more and more popular in North America, and are well established in Europe, it is desirable to have the service temperature of many heat exchangers, such as intercoolers and charge air coolers, well over 200°C. Therefore, there is an increasing demand of high strength core alloys designed for service between 200 and 300°C. The development of high strength core alloys also helps the weight reduction in low temperature applications, since higher strength materials enable thinner gauge tube walls.

The major strengthening mechanism in aluminum core alloys is the solid solution hardening, mainly from the Mn and Cu alloying elements. Commercial high strength core alloys for long life brazing sheets contain up to ~1.5 wt.% Mn and ~0.6 wt.% Cu [1,2]. Due to the low solubility of Mn and Cu in aluminum, it is not possible to further increase their levels. Higher Mn and/or Cu contents will be

ineffective to improve the strength, meanwhile they may reduce the formability and sometimes the corrosion resistance. Magnesium is a unique alloying element in aluminum alloys. It not only has high solubility and strong solid solution hardening effect, but also increases the sheet formability. However, in general the Mg level in brazing sheet core alloys is controlled to be below 0.5 wt.%, because in the flux brazing process, which is the most widely used brazing technology, Mg diffuses to the sheet surface and reacts with the fluxing salt, forming detrimental coarse needle-like compounds which adversely affect the ability to form a good joint. The other two major brazing technologies, vacuum and nickel brazing, are not sensitive to Mg and thus they tolerate higher content of Mg.

The objective of the present work is to develop new high-strength brazing sheet core alloys for vacuum brazing and nickel brazing applications. The new alloys should be able to maintain 60 MPa YS at service temperatures close to 300°C, without affecting the sheet formability and corrosion resistance, or leading to significant increase in material and/or processing costs.

EXPERIMENTS

Four new alloys were designed with increasing Mg content from 0.5, 1.0, 1.5 up to 2.0 wt.%, based on a commercial brazing sheet core alloy containing 1.5 wt.% Mn, 0.5 wt.% Cu, 0.1 wt.% Mg, and relatively low levels of impurity Fe and Si. The nominal compositions are listed in Table 1, where the commercial alloy is labeled Alloy-1 and the newly designed alloys, 2 to 5. The alloys were cast by DC casting and the ingot size was 24" by 9" by 3.75". Al-Ti-B grain refiner was used in ingot casting and the level of Ti in melt was controlled to be 0.01 wt.% in Alloys-1 to 3, 0.014 wt.% in Alloy-4 and 0.018 wt.% in Alloy-5. The ingots were scalped by ~10 mm on each rolling face, leaving a thickness of ~75mm, re-heated in air from the room temperature to 520°C with 50°C/h heating rate, soaked for 6.5 - 7 hours, then hot rolled to a gauge of 4.8 - 5mm in a reversing mill with 18" diameter rolls. The exit temperature of hot rolling was about 270 to 295°C. After cooling down to the room temperature, the hot rolled bands were further cold rolled down to the final gauge of ~1mm using the same rolling mill. The final gauge cold rolled sheets were batch annealed at ~290°C for 2 hours with 50°C/h heating rate and air cooled to reach the H24 temper, then gone through a simulated brazing cycle at 590°C for 10 minutes in an air furnace, followed by air cooling.

Table 1. Nominal compositions of the commercial and newly designed alloys (wt.%).

Alloy	Mn	Cu	Mg	Fe	Si
1	1.5	0.5	0.1	0.25	0.1
2	1.5	0.5	0.5	0.25	0.1
3	1.5	0.5	1.0	0.25	0.1
4	1.5	0.5	1.5	0.25	0.1
5	1.5	0.5	2.0	0.25	0.1

The microstructures in different stages of sheet processing were characterized by optical microscope and scanning electron microscope (SEM) in the longitudinal sections. The tensile properties were determined on the final gauge post-brazing sheets, and the specimens were machined along the rolling direction (RD) according to the ASTM A-694 0.75" gauge length tensile specimen drawing. The testing was done at both the room temperature and elevated temperatures, i.e., 177, 215, 235, 260 and 288°C, with a constant cross-head speed of 0.75mm per minute. To assess the loss of strength upon long time exposure at service temperatures, post-brazing specimens were soaked in an air furnace at 177, 215, 235, 260 and 288°C for 2 weeks, separately, then tested at the same temperatures. The corrosion resistance was estimated by open circuit potential (OCP) test against a saturated calomel electrode at the room temperature in an acidic salt water. The specimens, 98mm by 24mm, were cut from the post-brazing final gauge sheets. A hole was drilled at one end of each specimen for electrical connection with a copper wire. The specimens were then fixed in epoxy, only allowing part of the surface exposed to the test solution. Prior to measurements, the specimen surface was wet polished with a series of SiC papers up to 400 grit, rinsed in ultrapure deionized water and dried with pressurized air. Following cleaning, the dimensions of each coupon exposed to the electrolyte were measured to the nearest 0.01mm.

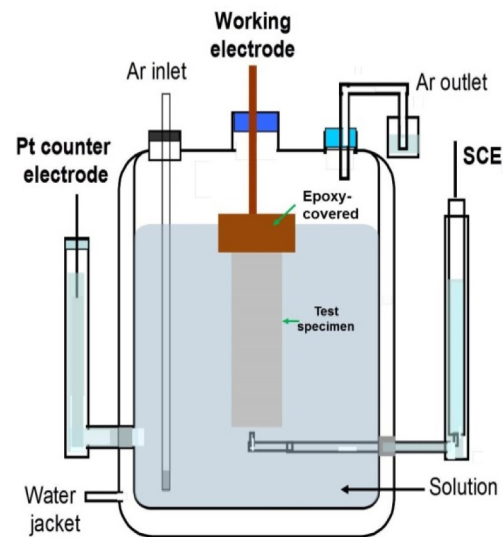


Figure 1. Schematic diagram of the cell used for electrochemical measurements.

As shown in Figure 1, open circuit potential (E_{OC}) and linear polarization resistance (R_p) measurements were conducted in a conventional three-electrode cell using a Solartron 1287 electrochemical interface equipped with a Solartron 1255 frequency response analyzer. A saturated calomel electrode (SCE) was used as a reference electrode and a platinum sheet as the counter electrode. For the linear polarization resistance measurements, a signal with an amplitude of ± 15 mV was superimposed on the specimen. The measurements were conducted in 35 g/L NaCl solution containing 0.01 M acetic acid (pH = ~3.4). All solutions were prepared with deionized water and analytical-grade reagents. The corrosion test lasted for 1 week, while EOC was continuously recorded and R_p was measured each 24 hours. The specimens after the test were rinsed and dried, and the surface morphology was characterized by optical

microscope and SEM. The number of pits with a diameter over 10 μ m and the largest pit dimension were determined by using SEM in an area of 6.75mm² for each specimen.

RESULTS

There were no difficulties experienced in DC casting, except that there was a tendency of minor hot cracking in the bottom part of ingot in high Mg Alloys-4 and 5. The Ti level was increased to 0.014 wt.% and 0.018 wt.% for Alloys-4 and 5, respectively, to decrease the casting grain size, redistribute the stress, and thereby prevent the hot cracking. After re-heating the grain size was $\sim$ 500 μ m in Alloys-1 to 3, while it reduced to $\sim$ 300 μ m in Alloys-4 and 5 due to the higher Ti addition. The major intermetallic phases observed under SEM in ingots after re-heating were the Al₆(Fe,Mn) phase in dendrites and fine Al₆Mn phase as dispersoids (Figure 2). Hot rolling and cold rolling were not difficult, but some edge cracking occurred in Alloys-2 to 5 during hot rolling and the tendency increased with the increasing Mg level.

The final gauge sheets after brazing cycle had a significant increase in both the YS and ultimate tensile strength (UTS) with the increasing Mg level in room temperature testing. As shown in Figure 3, 1 wt.% Mg gives $\sim$ 26 MPa in YS and $\sim$ 53 MPa in UTS. Meanwhile, the total tensile elongation keeps around 25% regardless of the Mg level (not shown in Figure 3). Figure 4 shows the YS and UTS of post-brazing sheets tested at the elevated temperatures from 177°C to 288°C. The contribution of Mg to YS remains strong, such that even at 288°C, 1 wt.% Mg still gives $\sim$ 19 MPa in YS, which is very effective in aluminum alloys. However, the increase of UTS, which is controlled by work hardening, is less affected by the Mg level at elevated temperatures. After exposure at the elevated temperatures for 2 weeks, the high temperature strength as a function of the Mg level has the similar tendency to Figure 4, but drops slightly (Figure 5).

Table 2. The polarization resistances of Alloys-1 and 5 after exposure in the test solution for various times.

Alloy	Polarization Resistance (R_p , ohms*cm ²)						
	24 h	48 h	72 h	96 h	120 h	144 h	168 h
1	3369	3274	3246	3313	2964	2833	3539
5	2963	3890	3444	3472	3393	3156	3610

Preliminary corrosion test results indicate that the addition of Mg up to 2 wt.% does not markedly affect the corrosion resistance. As shown in Table 2, in the test solution active corrosion occurred on the alloys due to their low polarization resistances, and the polarization resistances are very close, i.e., the addition of Mg has no significant influence. The Eoc (volt vs SCE) after 168 hours exposure is -790 mV for Alloy-1, which contains 0.1 wt.% Mg, and -800 mV for Alloy-5, which contains 2 wt.% Mg. The specimens after corrosion test show both general corrosion and localized pitting under optical microscope and SEM (Figure 6). Both the spatial distribution and size of pits are quite uniform. With the increasing Mg level up to 2 wt.%, the density of pits increases slightly but the size and depth of

pits remain nearly unchanged. The density of pits is 153 ± 22 per mm² for Alloy-1 and 176 ± 7 per mm² for Alloy-5, and the maximum pit diameter observed is 45 μ m in Alloy-1 and 42 μ m in Alloy-5.

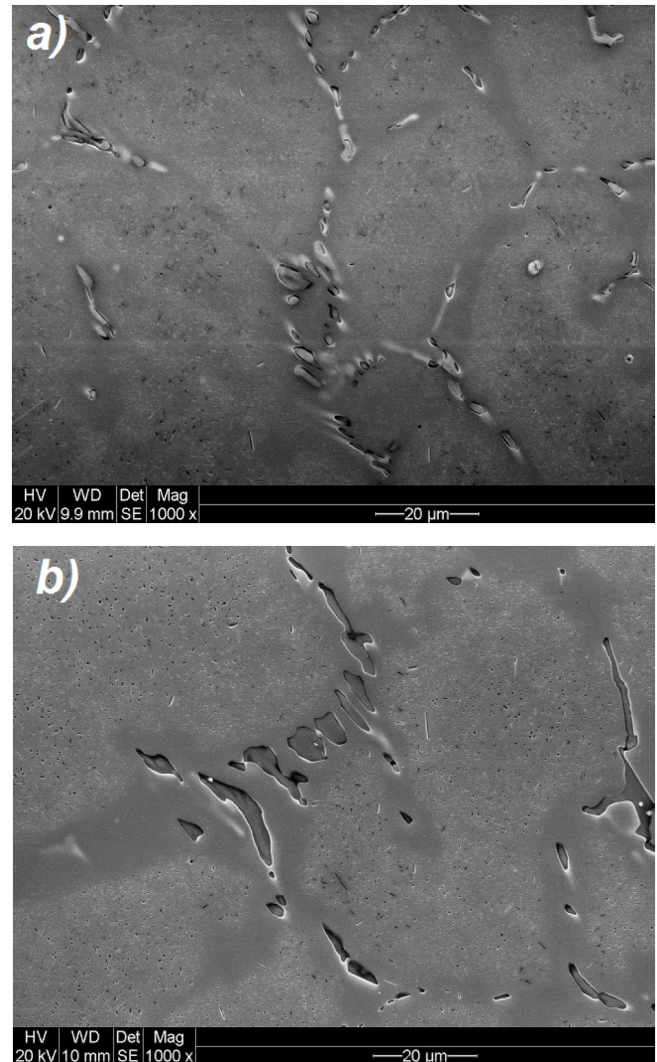


Figure 2. SEM images of ingots after re-heating showing the coarse Al₆(Fe,Mn) phase in dendrites and fine Al₆Mn dispersoid particles in aluminum matrix, a) Alloy-1 and b) Alloy-5.

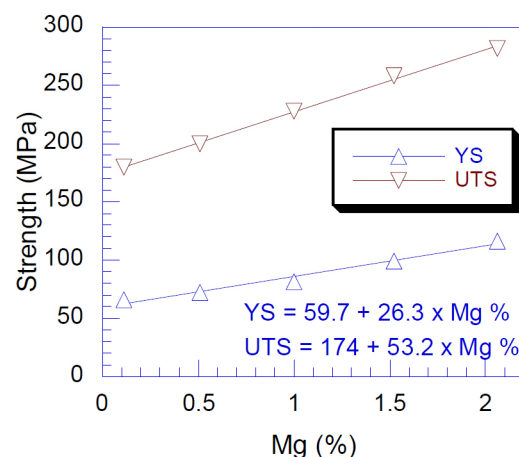


Figure 3. The YS and UTS of post-brazing sheets tested at room temperature.