Light Metals 2013 *Edited by: Barry Sadler*
TMS (The Minerals, Metals & Materials Society), 2013

EFFECT OF Zn CONTENT AND PROCESS PARAMETERS ON CORROSION BEHAVIOUR OF TWIN-ROLL CAST ALUMINUM BRAZING ALLOYS

Murat DÜNDAR, Mert GÜNYÜZ, Cemil IŞIKSAÇAN, Anıl PASTIRMACI
ASSAN Aluminum A.Ş., D-100 Karayolu, Yayla Mah., Rüya Sok. No: 2, 34944, Istanbul, TURKEY

Keywords: twin-roll cast aluminum, corrosion, brazing

Abstract

Al – Mn alloys are used as fin materials in various brazing applications of automotive industry. With the addition of Zn, these materials become more prone to corrosion with respect to tube materials and behave sacrificial to protect whole structure. Centerline segregation (CLS), inherently existing feature of Twin-Roll Cast material, is believed to play a role on electrochemical behavior of aluminum alloys. The aim of this study was to reveal contribution of centerline segregation to the overall corrosion behavior of Zn bearing Al-Mn alloys. Influence of casting parameters on magnitude of CLS and Zn content of the alloy is correlated with the open circuit potential measurements and salt spray test results. Complementary studies that aim to elucidate corrosion mechanism operating at the scale of microstructural features was also carried out by employing metallographic techniques and SEM-EDS studies.

Introduction

With increasing production and consumption amounts, aluminum is the leader in the metallurgy of non-ferrous metals. In many cases aluminum replaces traditional materials like stainless steels and copper alloys. Development of applications for aluminum and its alloys, as well as the sustained rise in consumption can be attributed to several of its properties. Lightness, thermal conductivity, electrical conductivity, corrosion resistance etc. are main advantages of aluminum alloys [1-2]. Especially 3003 alloys are preferred materials for automotive applications such as heat exchangers.

One of the production techniques of sheet aluminum alloys is twin-roll casting (TRC). This production method has been used for almost 50 years in the aluminum industry. Commercial TRC aluminum alloys have narrow freezing ranges and are cast at moderate casting gauge (3). In TRC, molten metal is fed onto water cooled rolls, where it solidifies and then rolled. A wide range of thicknesses and widths can be produced by twin-roll casting. Processing cost of TRC is significantly lower when compared to conventional direct casting. On the other hand, TRC has some characteristic features. With the high cooling rate achieved through water cooled rolls, TRC materials have rapidly solidified surfaces. Related with that, these materials have smaller grain sizes on their surfaces than that of the center. Heterogeneous distribution of intermetallics, dispersoids and eutectic structures can be encountered through thickness (4-6).

It is a well-known fact that alloying elements have a strong influence on the properties of aluminum alloys. Especially, the effects of alloying elements on the Mn solubility in Al-based solid solutions were investigated (7-8). It was found that Fe and Si decreases the solubility of other elements and Cu enhances the decomposition of supersaturated solid solution. Size and the quantity of the precipitates can affect the properties of Al alloys through certain mechanisms. Grant et al [9], reports the different effects of second phases containing Mn, Zr, Fe or Cu on the corrosion of Al alloys. However, the effect of Zn content on the corrosion properties of 3003 Al alloy was rarely investigated.

In this study, the effect of Zn content and intermediate annealing temperatures on corrosion properties of three types of modified 3003 brazing alloys and the effect of casting parameters on CLS formation were investigated.

Experimental

CLS cannot be easily recognized at the final thickness and does not allow thorough investigations for the aimed purpose of present study. All microstructural transformations are completed during homogenization annealing and then, content of CLS is not altered down to final thickness. Therefore studies were conducted on the samples that were 60% cold rolled and then exposed to different intermediate annealing temperatures. Different annealing temperatures were applied, namely between 450^{0}C to 550^{0}C. Annealing operations were also performed in laboratory scale furnaces. Coils were cast with different Zn contents by twin-roll casting technology.

Table 1. Zn content and annealing conditions of modified 3003 Al alloys (HZ: high Zn content, LZ: low Zn content, Mod: Modified)

Material	Zn content (%)	Annealing condition (°C - h)
3003Mod.	-	450 – 8
3003Mod.	-	550 – 8
3003LZ	0,6 – 08	450 – 8
3003LZ	0,6 – 0,8	550 – 8
3003HZ	1,4 – 1,6	450 – 8
3003HZ	1,4 – 1,6	550 – 8

6x5cm^2 samples were taken from the materials exposed to processes prescribed above. Cross-section of samples were metallografically prepared for salt spray corrosion tests and placed in SWAAT corrosion test chamber (Ascott S120S). %5 NaCl solution was used as corrosive media with a flow rate of 15 ml/min at 35°C. (Pressure was 14 bar). Cross-sections of the samples with polished edges were observed with scanning electron microscope (SEM-JEOL 5600) along with energy-dispersive x-ray spectroscope (EDS-OXFORD 6587).

Another set of homogenized samples were rolled down to 0.1mm and back-annealed for H24 temper. Electro-chemical potentials (ECP) were measured by VersaSTAT 3 potentiostat according to ASTM G-69 standard. Test solution consisted of 58,5 g of NaCl and 9 mL of hydrogen peroxide reagent per 1 L of aqueous solution. Exposed surface area of test specimens was 430mm^2. Specimens were cleaned with acetone and distilled water in an ultrasonic cleaner for 5 minutes prior to test. Saturated calomel electrode was used as reference electrode.

Also samples having dimensions of 10x10 cm were cut from 3003Mod, 3003LZ and 3003HZ H24 materials at final gauge and hold in salt spray chamber for 40 days in order to observe the onset of corrosion visually.

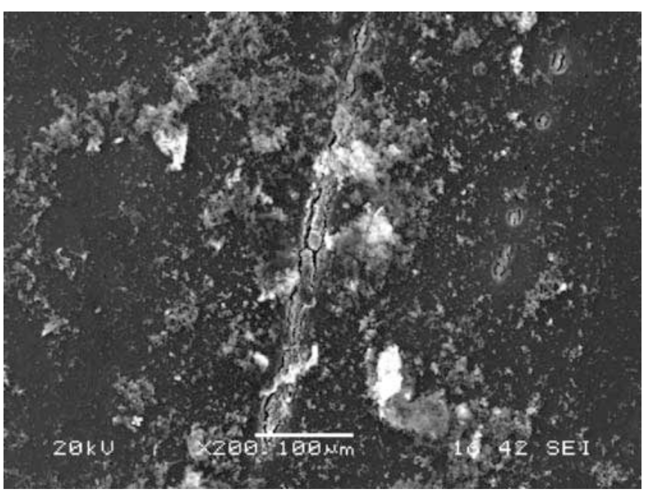
The effect of casting parameters such as casting gauge, casting speed and headbox temperature on CLS formation was also investigated. 3003HZ coils were cast at a thicker gauge with a lower speed (Table 2.) and as-cast samples of these coils were metallografically prepared and investigated with a light microscope in order to evaluate the effect of these parameters on magnitude of CLS which is thought to have a detrimental effect on the corrosion properties of Twin-Roll Cast materials.

Table 2. Set of casting parameters (Set A: standard parameters, Set B: modified parameters)

	Casting Gauge (mm)	Casting Speed (cm/min)	Headbox temperature (^oC)
Set A	Low	High	High
Set B	High	Low	Low

Results and Discussion

Homogenized 3003HZ samples were investigated by SEM after 24 hours of SWAAT test. Figure 1a reveals the material loss at the interface between intermetallic phases and surrounding matrix that bears Zn. Corrosion products that formed on the surface indicates the start of corrosion after 24 hours. Line scan EDS analysis given in Figure 1b indicates that intermetallic phases mainly consist of Al-(Fe-Mn-Si) and Zn is in solid solution.



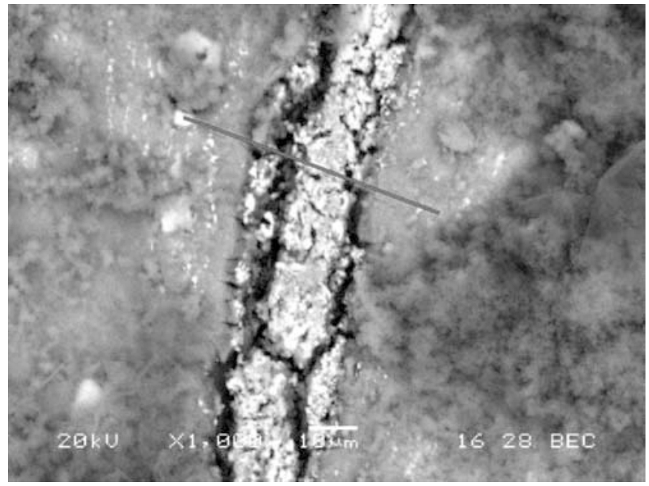


Fig 1a. SEM images of CLS of homogenized 3003HZ samples after 24h of SWAAT test

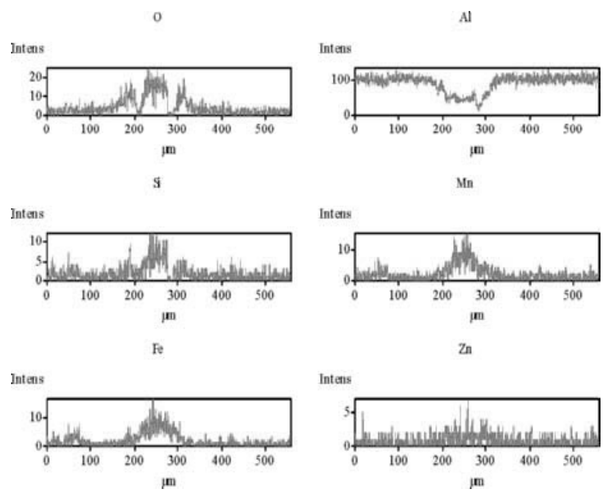


Fig 1b. Line scan EDS analysis of CLS of homogenized 3003HZ samples after 24 h salt spray test

The results of another set of samples on which intermediate annealing (450^{0}C) was applied, was also included to current study. The purpose was to see the influence of temperature on the morphology and composition of CLS.

SEM images of the samples with different Zn content and exposed to different annealing temperatures can be observed in Figure 2-3. Samples exposed to intermediate annealing after 60% reduction in thickness indicate that 3003Mod and 3003LZ exhibit superior corrosion performance compared to 3003HZ in salt spray test regardless of the annealing temperature applied. 3003LZ presents a similar behavior to 3003Mod. General macroscopic appearance and interaction of intermetallic constituents of Zn bearing 3003 alloys with corrosive media are in accord with these observations. Possible mechanism of corrosion observed is; cathodic behaviour of intermetallic phases with respect to the aluminum matrix that has Zn in solid solution results in first corrosion attack to the interface between particle and matrix. However this mechanism does not appear to operate so aggressively with 3003Mod and 3003LZ material due to the absence and shortage of Zn in the matrix, respectively.
Since 3003Mod does not contain any Zn, it will not behave sacrificial to protect tube materials in heat exchanger applications.

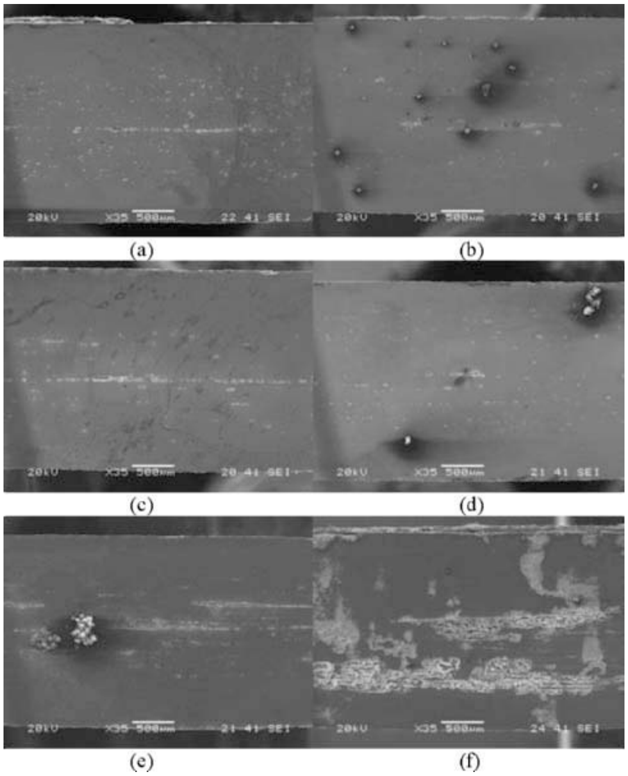


Fig 2. Low magnification SEM images of samples after 96h salt spray test with different Zn content annealed at different temperatures (a,b: 3003Mod; c,d: 3003LZ; e,f:3003HZ; a,c,e : annealed at 550^{0}C; b, d, f: annealed at 450^{0}C)

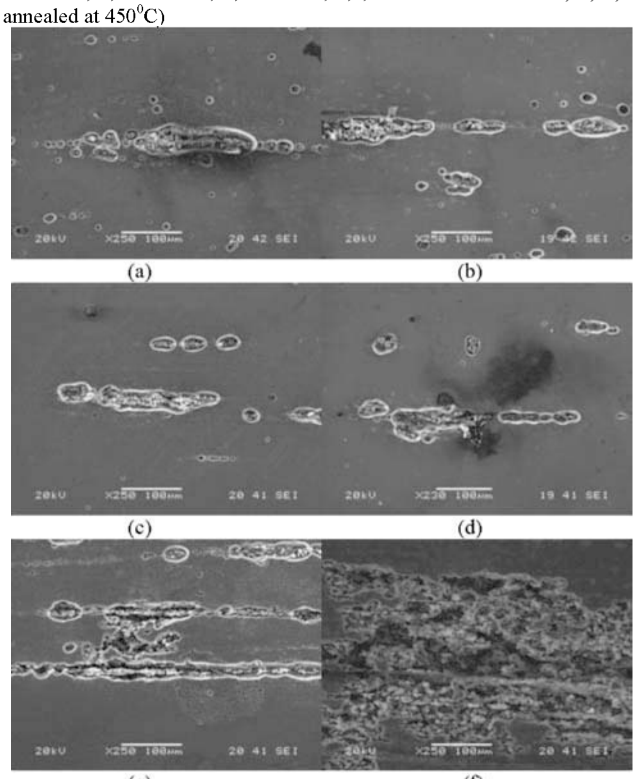


Fig 3. High magnification SEM images of samples after 96h salt spray test with different Zn content annealed at different temperatures (a,b: 3003Mod; c,d: 3003LZ; e,f:3003HZ; a,c,e : annealed at 550^{0}C; b, d, f: annealed at 450^{0}C)

SEM images shows that annealing temperature has a considerable influence on corrosion resistance of 3003 HZ samples bearing %1.4-1.6 Zn,whilst both samples without Zn (3003Mod) and bearing low Zn (3003LZ) stays unaffected. Annealing operation performed at 450^{o}C deteriorates corrosion resistance of 3003 HZ samples when compared with those annealed at 550^{o}C. Centerline segregations are preferential sites which are exposed to corrosion. Cathodic nature of intermetallic particles located on CLS operates more aggressive in case of high Zn amount depending on annealing temperature. Lack of required microstructural conversions encountered with annealing at a lower temperature has a detrimental effect on corrosion resistance. On the other hand, 3003 LZ samples performs similar to modified 3003 samples in terms of corrosion resistance regardless of the intermediate annealing temperature and ECP measurements verify these findings (Fig 4.). 3003HZ samples are less noble with respect to 3003Mod and 3003LZ samples.

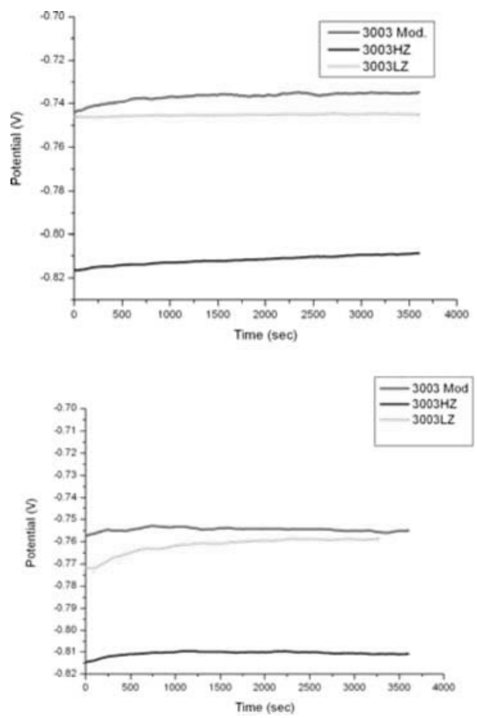


Fig 4. Electro-chemical potentials of the 3003Mod, 3003LZ and 3003HZ

Salt spray test of 0.1 mm materials are also in accord with ECP measurements. 3003Mod and 3003LZ materials exhibit no sign of corrosion after 40 days whereas 3003HZ materials corrode after 14 days. However, effect of annealing temperature observed at samples with polished edges is not pronounced in ECP measurements and salt spray tests.

CLS formation, which is an inherent characteristic of TRC materials, was found to be considerably dependant on casting parameters such as casting gauge, casting speed and headbox temperature. Casting at a thicker gauge along with decreased casting speed and headbox temperature (Table 2.) had a positive effect in terms of reducing the magnitude of CLS (Figure 5.). Such an improved microstructure with less macro-segregation will also impove the corrosion behaviour of TRC materials due to the decrease in number of preferential areas which are observed to initiate the corrosion mechanism.

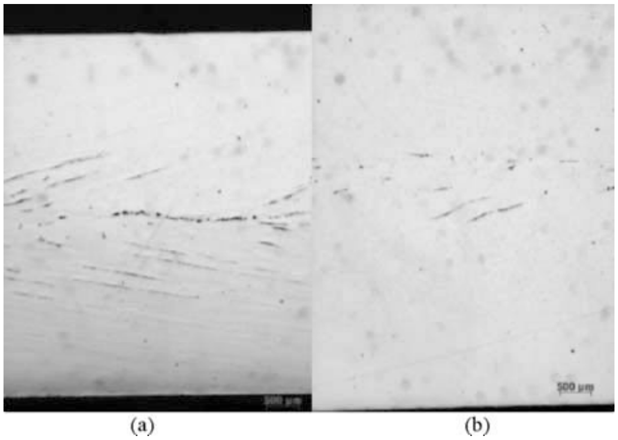


Fig 5. Cross-sections of as-cast samples a) Set A b) Set B

Conclusion

Centerline segregations, which are preferential areas in corrosion failure, play an important role on the electro-chemical behavior of TRC materials. Increasing Zn content leads to more negative ECP values. In presence of high Zn amount, annealing temperature also plays an important role on the interaction between intermetallic phases and Zn-bearing matrix.

- Increasing Zn content has a negative effect on corrosion resistance of 3003 brazing alloys with the presence of CLS.
- 3003Mod alloy is more noble with respect to Zn-bearing modified alloys, 3003LZ and 3003HZ.
- 3003LZ exhibits a similar behavior to 3003Mod alloy in salt spray tests both after 60% reduction in thickness and after annealing at final gauge (0.1mm) and they are both superior to 3003HZ in terms of corrosion resistance.
- 3003Mod and 3003LZ materials at final gauge (0.1mm) last for 40 days in salt spray chamber whereas 3003HZ corrodes after 14 days.
- Possible mechanism of corrosion observed is; cathodic behaviour of intermetallic phases with respect to the aluminum matrix that has Zn in solid solution results in first corrosion attack to the interface between particle and matrix.
- On the samples after applying 60% reduction in thickness, annealing temperature considerably affects the corrosion behavior of 3003HZ alloy, whilst 3003Mod and 3003LZ stay unaffected. 3003HZ samples annealed at 450°C are inferior to that annealed at 550°C. However same effect could not be observed at final thickness both with ECP measurements and salt spray tests.
- Modifying casting parameters such as casting gauge, casting speed and headbox temperature was found to eliminate CLS formation to some extent which will significantly improve corrosion resistance most likely.

References

[1] Vargel C, Corrosion of aluminum, Elsevier Ltd, Oxford, 2004

[2] Mei-jun Z, Dong-yan D, Effect of Zn content on tensile and electrochemical properties of 3003 Al alloys. Transaction of Nonferrous Metals Society of China, 2010, 2118 – 2123.

[3] Yun M, Lokyer S, Twin roll casting of aluminium alloys, Materials Science and Engineering A, 2000, 116 – 123.

[4] Keles O, Dundar M, Aluminium foil: Its typical quality problems and their causes, Journal of Materials Processing Technology, 2007, 125 – 137.

[5] Haga T, Tkahashi K, Twin roll casting of aluminium alloy strips, Journal of Materials Processing Technology, 2004, 42 – 47.

[6] Santos C A, Spim J A, Modeling of solidification in twin roll strip casting, 2000, 33 – 39.

[7] Goel D B, Furrer P, Precipitation in aluminium manganese (iron, copper) alloys, Aluminium, 2004, 511 – 513.

[8] Fernandes R C, Padilha A F, Effect of Mn and Fe contents on the microstructural evolution of two twin roll caster Al – Fe – Mn – Si alloy, 2008,165 – 169.

[9] moore K L, Sykes J M, Pitting corrosion of spray formed Al – Li – Mg alloys, Corrosion Science, 2008, 3221 – 3226.