An innovative class of aluminum alloys for automotive industry: investigation on their corrosion resistance

I Peter¹, C Castella² and R Molina³

¹University of Medicine, Pharmacy „George Emil Palade” din Targu Mures, Faculty of Engineering and Information Technology Science and Technology, N. Iorga street no.1, Targu Mures, Romania
²Politecnico di Torino, Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
³Teksid S.p.a. Via Umberto II, 5, 10022 Carmagnola TO, Italia

E-mail: ildko.peter@umfst.ro

Abstract. Self-hardening aluminum alloys (AlZn10Si8Mg, EN-AC-71100) represent an interesting innovative class of material for the production of automotive and aerospace components with high-mechanical strength and good corrosion resistance. The aim of the present is related to the investigation of the intergranular corrosion resistance of an innovative class of self hardening alloys. Microstructural characterization combined with compositional analysis has been carried out by Optical and Scanning Electron Microscope equipped with Energy X-rays Dispersive Spectroscopy unit. Three-point bending test and Charpy Impact test have been performed and the corrosion resistance of the alloys has been investigated according to standard BS 11846, method B. The susceptibility of the alloy to intergranular corrosion has been assessed evaluating the maximum corrosion depth and the weight loss of the alloy after corrosion test. The results obtained have been demonstrated that the corrosion resistance of the alloy can be achieved by Mg addition.

1. Introduction

Due to their very attractive properties the most commonly, employed light alloys for producing high stressed components in automotive and aeronautical applications are aluminium, magnesium and their alloys. Al-based alloys reveal high strength/weight ratio, good formability, excellent combination of castability and mechanical properties which associated to an excellent corrosion resistance and moderate production costs make them very challenging for a large variety of applications [1-3].

In the last decades, the content of aluminum in the production of cars is continuously increasing [4]. In 2012 the average amount of aluminum alloys, for a European car, has been situated around 140 kg as reported in [5]. This total content is mainly interest some components as: power-train, supporting frame, suspension arms and finally the car body [5].

The driving force for the development of new Al compositions and/or innovative technologies is related to the necessity to reduce the weight of the cars and consequently the CO2 gas emission, which is considered one of the most important greenhouse effect.

Even if high-pressure die casting (HPDC) is one of the most diffused technique accepted to produce Al based alloy components [6] the parts manufactured by this technology are affected by some intrinsic defects (gas and shrinkage porosities developed during the production) [7-8]. To avoid this difficulty
many new and different processes have been studied and developed during the years, but a large-scale industrial application still seems like a dream. Here one can mention some technologies, as modified squeeze casting, thixocasting, rheocasting, thixomolding, [7, 9-12] which are prevalently used for very high performance components, where mechanical resistance and excellent surface finishing properties are extremely important. For these reasons the cost related issues has been overlooked. The most important characteristic of this process belong to the use of the slurry with a thixotropic property: it can be handled like a solid, but when a shear stress is applied and the viscosity decreases dramatically it flows like a liquid. Semi solid metal processing technologies are a near net shape processes allowing to produce the final product with very fine and pore free microstructure avoiding any additional finishing operations, thus reducing the time needed for the production procedure.

One of the most important property for all the aluminum alloys is their good corrosion resistance, affected mainly by the presence of secondary phase [13] and of the grain boundaries precipitates [14]. These phases can be either more active or more noble than the surrounding solid solution Al matrix, so could behave anodic or cathodic with respect to the α-Al matrix and consequently can lead to the formation of micro-galvanic couples resulting in localized corrosion phenomena.

The corrosion phenomenon of aluminum and aluminum alloys is essentially an electrochemical process and can be considered, as a flow of electric current between anode and cathode. As concerns aluminum alloys, containing several types of intermetallic phases, the corrosion is mainly a microgalvanic process between intermetallic phases and the α-Al matrix. Hence is fundamental to know the electrochemical characteristics of these constituent particles. The chemical composition of intermetallic phases as well as their spatial distribution and density are all features that affect the level and the morphology of subsequent corrosion.

The intergranular corrosion resistance (IGC) is caused by the difference between the potential corrosion of precipitates, formed in the grain boundaries, and the matrix leading to the formation of microgalvanic cell.

IGC compared to pitting corrosion is a faster corrosion process, but an inferior depth can be reached, because of the limited transport of oxygen in the narrow corrosion path. Both IGC and pitting corrosion are deleterious and generally have a negative effect on the corrosion fatigue resistance of the alloys [15,16].

The intergranular corrosion resistance is mainly influenced by the heat treatments carried out and their effects on the morphology and size of the grain boundary precipitates. The chemical composition of both grain boundary precipitates and aluminum matrix are important too.

The self-hardening aluminum alloys families are an innovative and promising class of metallic alloys: their main feature is related to the achievement of high mechanical performance, without the need of any heat treatments, because they are subjected to a natural ageing at room temperature in about 7-10 days [16-20].

Some studies are still considering the behaviour of these alloys, but the data on their corrosion resistance capabilities are very limited.

In this research paper the intergranular corrosion resistance of the self hardening alloys has been considered and studied.

2. Experimental procedure

The chemical composition of the investigated self-hardening aluminum alloys, produced by die casting technique, is reported in the author previous paper [20]. Samples for the corrosion and the mechanical test have been obtained by extracting from the configuration reported in figure 1.

The thickness in the step casting is varying from 5 mm to 20 mm and consequently the cooling rate decreases from the zone close to the runner to zone close to the riser. This type of casting allows evaluating the effect of the cooling rate on the microstructure and consequently on the mechanical properties of the alloys.

The Mg addition promote the development of Mg₂Si precipitates, which are anodic with respect to the α-aluminum matrix and allow enhancing the corrosion resistance of the alloy [13,21].
The based self-hardening aluminum alloy (AlZn10Si8Mg/ EN-AC-71110) has a Mg content in the range of 0.3-0.5 wt%. Through modification of its chemical composition by addition of Mg up to 3 wt% can be considered as a possible solution to enhance its corrosion resistance. The alloys produced, with 1% and 3% of Mg, have been labelled as AlZn10Si8Mg1, AlZn10Si8Mg3, while the basic alloy is labelled as AlZn10Si8Mg. Optical microscope, (OM, MeF4 Reichart-Jung) and Scanning Electron Microscope (SEM, Leo 1450VP) equipped with Energy X-rays Dispersive Spectroscopy unit (EDS, Oxford microprobe) have been employed for their microstructural characterization.

The corrosion resistance of the alloys has been investigated according to standard BS 11846, method B reported in [22]. The corrosion test includes degreasing of the samples in acetone and ethanol, alkaline etching (5 min in 7.5 wt% NaOH at 55–60°C) followed by 24 h immersion in an acidified salt solution (30 g NaCl and 10 ml concentrated HCl per liter). Following to the immersion, the samples have been cleaned by water and ethanol washing and then have been dried. The susceptibility to intergranular corrosion (IGC) has been investigated evaluating the:
   a. maximum corrosion depth;
   b. weight loss.

The mechanical properties, before and after IGC corrosion test have been evaluated by three-point bending test (Dynamometer wick Z100 tool) and by Charpy test to monitor how the corrosion phenomenon affects the mechanical performances of the alloys.

### 3. Results and discussion

#### 3.1. Microstructure analysis

A typical casting microstructure made of α-Al dendrites and of Al-Si eutectic phase has been observed in figures 2-4. As expected, higher values of cooling rate allow obtaining in all cases a finer microstructure. The precipitation of large Mg based intermetallics, with a Chinese script morphology, is favoured by the highest content of Mg as well as by high values of cooling rate. The presence of Mg2Si hardening precipitates has been demonstrated in [18-19].
Figure 2. Microstructure of AlZn10Si8Mg self-hardening alloy at different cooling rates: (a) Sample D 3 °C/s, (b) Sample C 6°C/s, (c) Sample B 8°C/s and (d) Sample A 14°C/s (100x).

Figure 3. Microstructure of AlZn10Si8Mg1 self-hardening alloy at different cooling rates: (a) Sample D 3 °C/s, (b) Sample C 6°C/s, (c) Sample B 8°C/s and (d) Sample A 14°C/s (100x).

Figure 4. Microstructure of AlZn10Si8Mg3 self-hardening alloy at different cooling rates: (a) Sample D 3 °C/s, (b) Sample C 6°C/s, (c) Sample B 8°C/s and (d) Sample A 14°C/s (100x).
3.2 Corrosion resistance

Figures 5 and 6 show, respectively, the OM and the SEM microstructures of the transverse cross sections of the samples after corrosion test. The microstructures reveal the presence of localized corrosion developed principally at the interface between silicon particles and the α-Al, because Si particles act as local cathodes with respect to the α-Al phase according to [13].

![Figure 5](image1.png)  
**Figure 5.** Optical microstructure of the transverse cross section of corroded samples.

![Figure 6](image2.png)  
**Figure 6.** SEM microstructure and EDS results of the transverse cross section of corroded sample, showing Si particles that act as local cathodes with respect to the eutectic Al matrix.

Furthermore, the corrosion takes place at the interface between the Al-Fe-Mn intermetallics and the α-Al as reported in figure 7, since these intermetallic phases behave cathodic with respect to the Al-matrix. The cathodic effect of iron-compounds can be reduced by addition of [13]. No corrosion attack has been observed on the primary α-Al phase.

![Figure 7](image3.png)  
**Figure 7.** SEM microstructure and EDS showing Fe-intermetallic which act as local cathodes with respect to the eutectic Al matrix.
Increasing the Mg content up to 3 wt.% the more accentuated precipitation of the Mg-based intermetallics occur and they act as sacrificial anode with respect to the Al-matrix, as reported in figure 8. As Mg content increases the total amount of Mg$_2$Si hardening precipitates grows improving the corrosion resistance of the alloy [13, 21].

![Figure 8. SEM image of Mg-based compounds that act as sacrificial anode.](image)

The weight loss and the penetration depth have been monitored after IGC test. The results obtained as a function of the alloy analysed are reported in figures 9(a) and 9(b): AlZn10Si8Mg3 self-hardening alloy reveals the lowest values of both the weight loss and of the penetration depth confirming that an increase of Mg content is a viable solution, also from industrial point of view, to enhance the corrosion resistance of the based self-hardening aluminum alloy.

![Figure 9. Weight loss (left) and (right) penetration depth, measured after the intergranular corrosion test.](image)

### 3.3 Mechanical properties

How the corrosion phenomenon affects the alloy's mechanical performances has been detected by measuring their mechanical properties before and after corrosion test. For the AlZn10Si8Mg and AlZn10Si8Mg1 alloys a decrease of about 20% of the flexural stress at break has been obtained after corrosion (figures 10 (a), (b)). A sharp decrease for the flexural strain at break has been obtained, when Mg content increases for both situations, before and after the corrosion test as shown in (figures 10(c), (d)). This deterioration can be mostly attributed to the change in size and morphology of the Chinese script intermetallic phases, causing the embrittlement of the samples. The benefit of the higher Mg content is limited to 1%. Beyond this percentage, the development of the largest and non-homogeneously dispersed intermetallic particles negatively influences the ductile property of the alloys and as reported below a lower impact energy has been obtained, after the corrosion test.
The AlZn10Si8Mg1 alloy has the highest values of flexural stress at break, thanks to the presence of Mg2Si and MgZn2 hardening precipitates. Increasing the Mg wt%, the Mg-Si based intermetallics become larger, and consequently they contribute to the crack growths followed by the failure of the alloy. This is the reason why AlZn10Si8Mg3 alloy presents lower flexural stress at break values than those of the AlZn10Si8Mg and AlZn10Si8Mg1 alloys.

Impact test has been carried out on un-notched samples, to emphasize the effect of the microstructure, to get some estimation on the ductility of the alloys under conditions of rapid loading, on the contrary which occurs during three-point bending test. The results obtained confirm the sensitivity of the impact toughness to the microstructural variations associated to Mg addition, as reported in figures 11(a), (b). Both alloys with a higher content of Mg show a decline in impact properties. For all the three investigated alloys, samples coming from zone B have higher impact energy with respect to the impact energy of sample coming from of zone D. When the cooling rate decreases and Mg content increases, due to the development of a coarser microstructure with larger intermetallic particles, the impact energy of the samples considerably decreases. Therefore, as for the flexural stress and strain at break regards for the impact energy, large Mg-based intermetallics are resulted to be detrimental.

![Figure 10](image1)

**Figure 10.** Three-point bending tests, flexural stress at break results: a) before the intergranular corrosion test and b) after the intergranular corrosion test; three-point bending tests, flexural strain at break results: c) before the intergranular corrosion test and d) after the intergranular corrosion test.

![Figure 11](image2)

**Figure 11.** Charpy test results: a) before the integranular corrosion test and b) after the intergranular corrosion test.
4. Conclusions
In this research paper a self hardening Al alloy was considered and analysed. Apart from some considerations on its microstructural behaviour, some investigations were performed on how the intergranular corrosion proceeds and how these aspects influence the mechanical performances of the alloys. Mg addition, up to 3 wt%, was performed to enhance the corrosion resistance of the alloys. Since both Si particles and Fe compounds act as local cathodes with respect to the α-Al matrix, for all the three investigated alloys, the corrosion takes place at the interface between silicon particles and the α-Al and at the interface between Al-Fe-Mn intermetallics and the α-Al. As Mg content increases the corrosion resistance of the considered self-hardening aluminum alloys increases as well, due to the precipitation of Mg-based intermetallics, with a Chinese script morphology and of the development of Mg2Si hardening precipitates. These compounds are both anodic with respect to the Al matrix.

A decrease of the flexural stress and the flexural strain at break was registered after corrosion in the case of the alloys with lower Mg content, while the alloy with the highest Mg content has a similar behaviour before and after corrosion test. As for the impact energy concerns, more than 1% of Mg negatively influences the alloy ductile property, after corrosion, and lower impact energy was obtained prevalently due to the development of the large intermetallic particles.

5. References
[1] Cao X, Campbell 2003 J. Metall. Mater. Trans. A 34 1409–1420
[2] Kumar G, Hegde S., Narayan Prabhu K. 2007 J. Mat. Proc. Techn. 182 152–156
[3] Rosso M, Peter I, Villa R 2008 Solid State Phenomena 141-143 237-242
[4] Liu G, Müller D B 2012 J. Cleaner Prod. 35 108-117
[5] Hirsch 2014 J. Trans. Nonferrous Met. Soc. China 24 1995–2002
[6] Gunasegaram D R, Givord M, O’Donnell R G, Finnin B R 2007 Mat. Science & Eng. A 559 847-856
[7] Rosso M, Peter I, Molina R, Montedoro A, Tonno G, Claus P 2012 La Metallurgia Italiana 3 25-28
[8] Jin S, Yan F, Fan Z 2015 Mat. Sc. & Eng. A 626 165–174
[9] Lakshmi H, Vinay Kumar M C, Raghunath L, Kumar P, Ramanarayanan V, Murthy K S, Dutta P 2012, J. Trans. Nonferrous Met. Soc. China 20 700–710
[10] BoChao L, YoungKoo P, HongSheng D 2011 Materials Science and Engineering A 528 986-995
[11] Peter I, Rosso M, Bivol C 2009 Met. Int. 14 15-18
[12] Patel M, Mathew G C Rs, Krishna P, Parappagoudar M B 2014 Procedia Technology 14 149 – 156
[13] Arrabal R, Mingo B, Pardo A, Mohedano M, Matykina E, Rodriguez I 2013 Corrosion Science 73 342–355
[14] Svenningsen G, Hurlen Larsen M, Walmsley J C Halvor Nordlien J, Nisancioglu K 2006 Corrosion Science 48 1528–1543
[15] Corrosion of aluminum and aluminum alloys, edited by Davis J R, The materials information society (USA: ASM International) 313 p
[16] Scamans G M, Birbilis N, Buchheit R G 2010 Corrosion of Aluminum and its Alloys, (Oxford: Elsevier)
[17] Tillová E, Ďuriníková E, Chalupová M 2011 Acta Metallurgica Slovaca 17/1 4-10
[18] Tillová E, Ďuriníková E, Chalupová E, 2011 Mat. Eng. - Materiálne inžinierstvo 18 1-7
[19] Rosso M, Peter I, Castella C, Molina R 2013 Metall. Sc. & Techn. 31/1
[20] Rosso M, Peter I, Castella C, Molina R 2014 Proc. TMS Aluminum Committee at the TMS- Annual Meeting & Exhibition, February 16-20, 2014 San Diego, California, USA, Light metals 2014
[21] Peter I, Rosso M, Castella C, Molina R 2014 Mat. Sc. Forum 794-796 1221-1226
[22] Kiryl A. Yasakau, Mikhail L. Zheludkevich, Sviatlana V. Lamaka, 2007 M.G.S. Ferreira Electrochimica Acta 52 7651–7659
[23] Determination of resistance to IGC of solution heat-treatable aluminium alloys, 1995, Standard BS11846:1995, British Standards Institution