Intergranular Corrosion of Extruded AA6000-Series Model Alloys

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Keywords: AIMgSi alloys, intergranular corrosion, Q-phase

Abstract

Susceptibility to intergranular corrosion (IGC) of 6000-series model alloys extruded in the laboratory was investigated as a function of Cu content, cooling rate after extrusion and artificial aging. One alloy type contained about 0.6 wt% each of Mg and Si with varying Cu content. The second type was a Cu-free alloy with higher Si content (*ca.* 1%). Extrusions with low Cu content (≤ 0.02 wt%) were resistant to localised corrosion, while those with high Cu content (0.17 wt%) could become susceptible to IGC. FE-SEM investigation revealed large grain boundary precipitates on air cooled samples. These precipitates were Mg₂Si and Q-phase (Al₅Cu₂Mg₈Si₆) in the samples susceptible to IGC. Only Mg₂Si was present in the corrosion-resistant samples. IGC susceptibility was attributed to the microgalvanic coupling between the noble Q-phase particles and the adjacent depleted zone. IGC can be prevented by proper heat treatment.

1. Introduction

IGC is the result of microgalvanic processes along grain boundaries [1,2]. Galvanic coupling between the grain boundary particles and the matrix, grain boundary particles and the adjacent depleted zone, or between matrix and the depleted zone may result in preferential corrosion along the grain boundary. The grain boundary precipitates that cause IGC in aluminium alloys are usually nobler than the adjacent depleted zone produced, such as CuAl₂ and Al_xCu_xMg in AlCu alloys [1,2]. However, precipitation of active grain boundary phases, such as Mg₂Al₃, MgZn₂ and Al_xZn_xMg in AlMg and AlZnMgCu alloys, is also attributed to IGC susceptibility [1,2]. In this case the depleted zone is noble relative to the grain boundary phases.

AlMgSi alloys are generally regarded as highly corrosion resistant [1-3]. However, it is known that unfavourable alloying and thermomechanical treatment may introduce susceptibility to IGC [1,4]. Alloys with Si excess relative to the Mg₂Si stoichiometry may become susceptible to IGC, while those with Mg excess may exhibit pitting rather than IGC [3-5]. IGC susceptibility in the excess Si alloys is probably caused by an active depleted zone, adjacent to pure Si precipitates at the grain boundaries [3]. The presence of a continuous film of Mg₂Si in the grain boundaries may also introduce IGC susceptibility [3].

In addition to Mg and Si, other alloying elements may affect the corrosion performance of AIMgSi alloys, *e.g.*, the corrosion resistance decreases when the Cu content increases [3,6-11]. However, if the Cu content is kept below a certain value (0.1 wt%), the corrosion

properties are not appreciably affected [7,8]. It was also reported that this critical level can be as high as 0.4 wt.% [3]. Limited amount of information is available on the IGC mechanisms of AIMgSi alloys with Cu additions, even though the effect of Cu is well known. IGC susceptibility was related to the presence of SiCu and AIMgSiCu grain boundary precipitates [12-14], and microgalvanic coupling between these particles and the adjacent depleted zone. Q-phase ($AI_5Cu_2Mg_8Si_6$) was observed on the grain boundaries of alloy 6111 [15] and several model AICuSiMg alloys [16]. Q-phase grain boundary precipitates were also observed in the heat affected zones formed during welding of 6005 [17].

For materials susceptible to IGC, the occurrence of IGC increases during artificial aging and is highest at peak hardness [1,4,18-20]. Further aging (overaging) may reduce or remove this susceptibility [4,12-14,21-23]. This was related to coarsening of grain boundary precipitates along with particle growth in the matrix. As a result, the compositions of the depleted zone and matrix become similar and reduce the difference in the corrosion potential [12]. At the same time, coarsening of grain boundary precipitates transform continuous grain boundary precipitates to discrete particles, another possibility for reducing IGC susceptibility.

Limited information is available on how cooling after extrusion affects the corrosion performance of AIMgSi alloys. Slow cooling by air is known to cause large grain boundary precipitates [1], which may be detrimental for the resistance to IGC.

The objective of this work was to investigate the effect of Cu content, cooling rate and aging on IGC susceptibility of AIMgSi alloy extrusions, with emphasis on the resulting microstructural changes.

2. Experimental

The chemical compositions of the alloys studied in this work are given in Table 1. Alloys A and B are two variants of the same alloy containing different levels of Cu. Alloy C is a virtually Cu-free material with higher alloying contents of Si and Mn relative to the previous two alloys.

Alloy	Mg	Si	Fe	Mn	Cu	Cr	Ti	Zn	AI	Mg:Si ratio
А	0.55	0.60	0.20	0.15	0.17	0.02	0.01	0.02	Balance	0.92
В	0.54	0.60	0.22	0.15	0.02	0.03	0.01	0.01	Balance	0.90
С	0.57	0.93	0.20	0.59	0.0005	0.001	0.01	0.006	Balance	0.61

Table 1: Compositions of model alloys studied in this work [wt%].

The extrusion was performed in an 8 MN laboratory press with a reduction ratio of 34:1. The billets were solution heat treated prior to extrusion. The cross section of the extruded flat profiles was 2.7 x 78 mm. The extruded profile was either quenched in water directly after die exit or cooled in air at ambient temperature. Sections of the extruded profiles were artificially aged to the T6 temper, or they were used in the naturally aged T4 temper. The samples referred to be in the T6 temper actually were artificially aged after extrusion without repeating the solution heat treatment. The same restriction applied to the T4 material. Thus, a total of 12 different sample variants for characterisation and corrosion testing was obtained. It should be emphasized that the T4 temper is generally not of commercial interest. Use of samples of this temper was nevertheless deemed necessary in this study for a better understanding of the effect of thermal history on IGC.

The corrosion testing was performed according to the British standard BS-ISO 11846, method B. This test involved degreasing, alkaline etching (3 min in 7.5 wt% NaOH at 55-60 °C) and 24 h immersion in acidified NaCl solution (30 g NaCl and 10 ml concentrated HCl per litre at 25 °C). The corrosion susceptibility was evaluated visually from cross sections of corrosion tested material examined in optical microscope.

The effect of heat treatment on IGC susceptibility was further investigated using the air cooled T4 variant, which showed the highest susceptibility. First these samples were solution heat treated (30 min at 545 °C) in a salt bath. Subsequently they were moved to another salt bath at a different temperature (between 250 to 500 °C), kept there for a certain time (varied from 10 to 10 000 s), and finally quenched in water. The heat treated samples were then corrosion tested as previously described. It should be emphasized again that this sort of heat treatment procedure is uncommon in practice. The objective of this research work was to gain insight to the precipitation mechanisms and resulting corrosion behaviour by using controlled heat treatment.

Both as-extruded and electropolished samples were used for field emission scanning electron microscopy (FE-SEM) investigation. The latter type was prepared by grinding, polishing through 1 μ m diamond paste and finally electropolishing in a solution containing 2 parts by volume methanol and 1 part HNO₃. Electropolishing was performed at an applied potential of 12 V for 2 min, and the temperature was maintained between -32 and - 37 °C by cooling with liquid nitrogen. The samples were washed with ethanol directly after electropolishing and then dried.

Foils for transmission electron microscopy (TEM) investigation were obtained from the near surface and centre of the profiles. They were prepared in the standard manner by electrolytic thinning. TEM was operated at an accelerating voltage of 300 kV.

3. Results

The data summarised in Table 2 indicate corrosion only of Alloy A (higher Cu content), whereas the samples with low Cu content (alloys B and C) were essentially resistant to localised corrosion (IGC and pitting). Cooling rate and aging had significant influence on the corrosion performance of the high Cu Alloy A, as shown in Figure 1.

Water quenched Alloy A samples were essentially resistant to localised corrosion. However, these samples exhibited pitting corrosion and some IGC after artificial aging. Air cooled Alloy A samples were susceptible to IGC. However artificial aging reduced IGC and corrosion became more localised and more pitting type than IGC.

Microstructure investigations by SEM and TEM revealed significant grain boundary precipitation in all air cooled samples (Figure 2a), while no grain boundary precipitates were present in the water quenched samples (Figure 2b). Artificial aging introduced small grain boundary particles in the water quenched samples (not shown), while no changes could be observed on the grain boundaries of air cooled samples as a result of aging.

EDS analysis, both in SEM and TEM, indicated grain boundary precipitates of Mg_2Si and Q-phase ($Al_5Cu_2Mg_8Si_6$) on the Alloy A samples, while only Mg_2Si were found on alloys B and C. The presence of Q-phase could be confirmed from selected area diffraction patterns (not shown), which matched the reported crystal structure of the Q-phase

(hexagonal, a = 1.03 nm and c = 0.405 nm [1]). The small size of grain boundary precipitates in water quenched T6 samples rendered elemental analysis difficult. However, EDS analysis in FE-SEM indicated the presence of Q-phase in Alloy A and only Mg₂Si in alloys B and C.

Table 2: Results from accelerated corrosion testing according to BS-ISO 11846 and EDS analysis of grain boundary precipitates.

Alloy	Cu cont.	Mg:Si	Cooling- and aging	Dominating corrosion mode	Grain boundary	
	[wt%]	ratio	variant	maximum corrosion depth [particle type	
А	0.17	0.92	Air cooled T4	Uniform IGC	560	Q-phase, Mg ₂ Si
Α	0.17	0.92	Air cooled T6	Scattered IGC attacks	265	Q-phase, Mg ₂ Si
Α	0.17	0.92	Water quenched T4	Slight corrosion	100	-
A	0.17	0.92	Water quenched T6	Pitting and localised IGC	200	Probably Q-phase
В	0.02	0.90	Air cooled T4	Slight corrosion at surface	60	Mg₂Si
В	0.02	0.90	Air cooled T6	No localised corrosion	25	Mg ₂ Si
В	0.02	0.90	Water quenched T4	No localised corrosion	< 15	-
В	0.02	0.90	Water quenched T6	No localised corrosion	15	Probably Mg ₂ Si
С	0.0005	0.61	Air cooled T4	Slight corrosion at surface	50	Mg₂Si
С	0.0005	0.61	Air cooled T6	No localised corrosion	< 15	Mg ₂ Si
С	0.0005	0.61	Water quenched T4	No localised corrosion	< 15	-
С	0.0005	0.61	Water quenched T6	A few very small pits	35	Probably Mg ₂ Si









a) Air cooled T4

Figure 1: Cross sectional images of corrosion tested Alloy A.



Figure 2: Backscatter FE-SEM images of the microstructure of Alloy A. The samples were electropolished to reveal the microstructure.

The results from corrosion testing of Alloy A after salt bath heat treatment are plotted as a function of heat treatment time and temperature in Figure 3. Uniform corrosion (crystallographic etching), IGC and pitting were the corrosion modes observed. Each corrosion type formed its own temperature-time domain, as illustrated in Figure 3.

IGC susceptibility of slowly cooled extrusions could be simulated by heat treatment of Alloy A extrusions at temperatures below 400 °C (Figure 3). Even as little as 10 s at temperatures from 350 to 250 °C introduced IGC susceptibility, while no IGC was

observed after direct water quenching of solution heat treated samples. Parallel to aging of air cooled Alloy A extrusions, prolonged heat treatment reduced the IGC susceptibility and finally introduced pitting. In a region characterised by heat treatment temperatures lower than 350 °C and times longer than 100 s, Alloy A was resistant to localised corrosion.



Figure 3: Time temperature transformation diagram (TTT diagram), showing the dominating corrosion mode in Alloy A as a function of temperature and heat treatment time.

4. Discussion

In summary, the results clearly show the effect of Cu on the corrosion resistance of the AIMgSi alloys. Effect of heat treatment, especially the cooling rate after extrusion and subsequent aging of Cu containing Alloy A, was also demonstrated. The low Cu alloys B and C had excellent corrosion resistance irrespective of the Mg:Si ratio, quenching and temper conditions.

Even though present in large quantities in the low Cu samples, discrete Mg_2Si precipitates at the grain boundaries did not introduce IGC-susceptibility. This may be related to the fact that Mg decreases and Si increases the corrosion potential of aluminium [2], and their simultaneous precipitation does not create a significant gradient of corrosion potential between the depleted zone and the solid solution matrix. Moreover, the Mg_2Si particles themselves are known to become electrochemically passive as a result of selective dissolution of the Mg component and formation of a SiO₂ layer [24].

Susceptibility to IGC must be the result of Q-phase grain boundary precipitates, because their presence was the only major difference between the resistant and the susceptible samples. The zone adjacent to Q-phase particles is expected to be depleted in Mg, Si and Cu. Depletion of Cu is known to decrease the corrosion potential significantly [2]. Thus, a potential gradient and microgalvanic coupling is established between the depleted zone (anode) and the Q-phase (cathode).

While the mechanism of IGC in air cooled Alloy A seems quite clear, the reduced IGC susceptibility by artificial aging is not yet understood. If there is a continuous network of noble grain boundary precipitates, coarsening to more discrete particles may be a possible

explanation. Another explanation may be the precipitation of MgSi phase(s), possibly covering the Q-phase precipitates and thus reducing their effect as cathodes. A third possibility is that particle precipitation and growth during aging may reduce the amount of alloying elements in solid solution such that the depleted zone and the matrix attain similar compositions. Work is in progress to test these hypotheses.

The water quenched samples in the T4 condition were not susceptible to IGC because no grain boundary precipitates were present. Increased IGC susceptibility of samples in the T6 condition must again be the result of grain boundary precipitation. In the T6 condition, air cooled and water quenched samples have essentially the same corrosion behaviour, characterised by limited, localised IGC and increased pitting.

5. Conclusions

- The effect of Cu on the corrosion resistance of AIMgSi alloy extrusions is once more documented. The present materials investigated (*ca.* 0.6% Mg and 0.6% Si) with high Cu content (0.17 wt%) can become susceptible to IGC, while those with lower Cu content (≤ 0.02 wt%) were resistant to localised corrosion. The corrosion performance of the high-Cu extrusions was greatly affected by cooling rate after extrusion and aging.
- Slow cooling after extrusions caused significant precipitation of Q-phase (Al₅Cu₂Mg₈Si₆) and Mg₂Si particles along the grain boundaries. The Mg₂Si phase was the only grain boundary precipitate present in low Cu samples. No grain boundary precipitates were found in water quenched samples.
- Samples, which had only Mg₂Si as grain boundary precipitates, were resistant to localised corrosion independent of the Mg:Si ratio, quenching rate and temper.
- IGC is caused by microgalvanic coupling between noble Q-phase precipitates at the grain boundaries and the adjacent depleted zone. By T6 treatment the IGC resistance of the susceptible air cooled material was improved, while that of the resistant water quenched samples was reduced, bringing the behaviour of the two variants closer to one another.
- IGC of 6000-series extrusions can be avoided, either by proper heat treatment, or by reducing the copper content.

Acknowledgements

This work was part of a Norwegian national research program entitled "Light Metal Surface Science", supported by The Norwegian Research Council, Hydro Aluminium, Profillakkering AS, Norsk Industrilakkering AS, NORAL AS, Jotun Powder Coatings AS, Electro Vacuum AS, DuPont Powder Coatings and GSB.

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