Effect of mechanical treatment on intergranular corrosion of 6064 alloy bars

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Abstract. Aluminium Al-Mg-Si-type alloys (6xxx-series) exhibit good mechanical properties, formability, weldability and good corrosion resistance in various environments. They often find use in automotive industry and other applications. Some alloys, however, particularly those with higher copper levels, show increased susceptibility to intergranular corrosion. Intergranular corrosion (IGC) is typically related to the formation of microgalvanic cells between cathodic, more noble phases and depleted (precipitate-free) zones along grain boundaries. It is encountered mainly in AlMgSi alloys containing Cu, where it is thought to be related to the formation Q-phase precipitates (Al₃Mg₅Si₂Cu₂) along grain boundaries. The present paper describes the effects of mechanical working (extrusion, drawing and straightening) and artificial aging on intergranular corrosion in rods of the 6064 alloy. The resistance to intergranular corrosion was mapped using corrosion tests according to EN ISO 11846, method B. Corrosion tests showed dependence of corrosion type on mechanical processing of the material. Intergranular, pitting and transgranular corrosion was observed. Artificial ageing influenced mainly the depth of the corrosion.

1 Introduction

Al-Mg-Si-type alloys (6xxx-series alloys) exhibit good mechanical properties, formability, weldability and good corrosion resistance in various environments. They frequently find use in automotive, aviation and other applications [1, 2]. Some of these materials are alloyed with copper to improve strength. In these alloys, particularly higher-copper alloys, increased susceptibility to intergranular corrosion (IGC) can be observed, most notably in unaged condition and less often in T6 temper condition. The effects of Cu as well as the opportunities for enhancing resistance to intergranular corrosion have received considerable attention in a number of studies [3-10]. Intergranular corrosion (IGC) is typically related to formation of microgalvanic cells between the cathodic more noble phases and the depleted (precipitate-free) zones along grain boundaries. It is encountered mainly in AlMgSi alloys which contain Cu, where it is thought to be linked to the formation of cathodic Q-phase (Al₃Mg₅Si₂Cu₂) along grain boundaries. The occurrence of phases along grain boundaries was observed using scanning transmission electron microscopy (STEM).

The impact of Cu addition and heat treatment on IGC was described in several papers [3-6]. The alloys contained 0.5-0.6% Mg, 0.6-0.8% Si, 0.2% Fe, 0.2% Mn and Cu at 0.02 through 0.7 wt. %. The occurrence of IGC was monitored in 2.5×78 mm² extruded flat bars. The effects of the cooling rate from the extrusion temperature were studied [3], as were the effects of artificial ageing [4, 5]. Corrosion tests were carried out according to EN ISO 11846. Corrosion was only monitored on the surface of the extruded parts. In an alloy with the Cu level of 0.02 %, no IGC was found. In an alloy with 0.2% Cu, IGC occurred in dependence on the artificial ageing time, and
changed into pitting corrosion. These findings suggest that between the occurrence of IGC and pitting corrosion, there is a region, in which no IGC occurs. Hence, overageing (by increasing either temperature or time) permits transition from the region with IGC to a region with suppressed IGC. The AA6056 material for aviation industry is used in overaged condition. It is supplied in the T78 state with enhanced resistance to IGC. According to the sources [7, 8], the T78 temper is achieved by two-stage ageing: 175 °C/6 h + 210 °C/5 h. In this research, the effect of thermomechanical treatment (extrusion, drawing, straightening and ageing) on intergranular corrosion in bars from EN AW-6064A (AlMg1SiBi) machinable alloy was studied. AlMgSi-type machinable alloys are used in automotive industry. Their improved machinability is imparted by alloying with Pb (6012 alloy) or with Bi+Pb (6262 and 6064 alloys). These alloys have higher alloy levels and contain more phases than the alloys studied in [3-10]. These phases include Bi and Pb cathodic particles. The resistance to intergranular corrosion was mapped using corrosion tests according to EN ISO 11846. Corrosion attack was observed on both the surface of the rods, and on the cross-section.

2 Experimental

The bars of 17 mm diameter were made by an industrial hot extrusion process using a multiple-hole die. The process temperature was 540–546 °C. Right after extrusion, the bars were water wave-cooled (T1 temper). The quenched bars were then drawn to the final diameter of 15 mm at 22 % reduction and straightened in Schumag straightening machine (T2 temper). The final operation was artificial ageing to T8 temper. Bars in conditions corresponding to each process step were gathered for testing. The chemical composition of the EN AW-6064A bars is shown in Table 1, the samples are listed in Table 2.

| Sample | Diameter | Temper | Description of thermomechanical processing |
|--------|----------|--------|-------------------------------------------|
| HA1    | 17 mm    | T1     | Extrusion, quenching                       |
| HB2    | 15 mm    | T2     | Extrusion, quenching, drawing              |
| HF     | 15 mm    | T2S    | Extrusion, quenching, drawing, straightening |

The bars were used in artificial ageing trials: single-stage and two-stage ageing from 160 °C/4h for underaged condition, to 180 °C/4h + 220 °C/4h for overaged condition. The progress of ageing was monitored by HV5 hardness measurement using DURASCAN 50 hardness tester. Tests of resistance to intergranular corrosion were conducted in accordance with the EN ISO 11846 standard, method B [12]. For these tests, specimens of 2 cm length were made from the bars. Their cut surfaces were ground with P-1200 grinding papers. The original surface of the bar was not altered. Before testing, the specimens were degreased in acetone. In accordance with the standard requirements, they were etched with 5 % NaOH solution at 55 °C for 2 minutes. After a water rinse, they were placed in concentrated nitric acid for cleaning. The test itself involved submerging in a test solution for 24 hours at room temperature. The solution was 30 g NaCl/litre solution + 10 ml concentrated hydrochloric acid. Metallographic sections were prepared on longitudinal cross sections through the specimens. The corrosion attacks on the bar surface as well as on the transverse cut surface were examined. The maximum corrosion depth was determined and documented using optical microscopy. The surfaces of specimens after corrosion testing were examined in JEOL JSM 6380 scanning electron microscope.
3 Results

3.1 Initial Microstructures
The microstructure of T8 temper bars upon drawing, straightening and ageing is shown in Fig. 1a. A micrograph of the phases is in Fig. 1b. The microstructure is fully recrystallized. The grains in the surface layer are relatively fine, with a size of 70 µm. In the centre, the grains are coarser, on the order of several hundred µm. Different grain sizes in the surface and in the interior are a typical occurrence in extruded bars from Al alloys. Typically, the surface layer contains coarse grains and the interior remains unrecrystallized [1, 2].

![Figure 1. Micrographs of grains and phases in HC samples upon drawing and ageing: a) electrolytically etched with Barker's reagent, polarised light, b) etched with Dix-Keller's reagent.](image)

The phases in the microstructure are banded and aligned in the extrusion/drawing direction. Large elongated particles consist of Bi or Bi+Pb. The small ones are alpha-Al\(_{13}\)(Fe,Mn,Cu,Cr)\(_3\)Si\(_2\) particles. Other small particles are Mg\(_2\)Si particles. The Bi, Pb and alpha-Al\(_{13}\)(Fe,Mn,Cu,Cr)\(_3\)Si\(_2\) particles are more noble, cathodic. The Mg\(_2\)Si particles are anodic. With cathodic particles, the matrix of the aluminium solid solution is etched away preferentially when placed in a corrosion environment. With anodic particles, they are the particles which are attacked. The microstructure may also contain cathodic Q-phase particles (Al\(_3\)Mg\(_2\)Si\(_3\)Cu\(_2\)). Figure 2b also shows minute particles along grain boundaries. EDS analysis revealed that they contain higher amounts of copper which suggests that they are Q-phase particles.

3.2 Corrosion tests of materials in initial condition
The initial condition evaluation was carried out on HF samples supplied in T2 (non-aged) condition. The surface corrosion is shown in Fig. 2.

![Figure 2. Corrosion attack in as-received bars HF, non-aged, a) surface, b) cross-section.](image)

The surface of the non-aged HF sample shows extensive intergranular corrosion (IGC) with a depth of more than 420 µm. On the cross-section through the HF specimen, IGC with a depth of approx. 500 µm was found as well.
3.3 Corrosion tests after aging of specimens of extruded bars HA1
Surface corrosion of selected specimens in variously aged conditions is illustrated in Figure 3. The corrosion of the transverse cut surface is shown in Figure 4. In specimens in underaged condition, the most extensive surface corrosion was found, involving continuous IGC with a maximum depth of more than 300 µm. In the peak-aged condition, the depth of attack decreased and IGC ceased to be continuous. In overaged condition, only sporadic pitting corrosion can be observed with a depth of about 120 µm.

![Figure 3. Corrosion on the HA1 bar surface after ageing: a) 180 °C/8h one-stage peak-aged, b) 160 °C/4h + 205 °C/4h two-stage peak-aged, c) 160 °C/4h + 220 °C/4h overaged. The same type of corrosion was found on the transverse cut surface. However, the corrosion depth was larger there: more than 400 µm. The only exception was the overaged sample where the depth was less than 100 µm.](image)

3.4 Corrosion tests after aging of specimens of drawn bars HB2
Surface corrosion of selected specimens in variously aged conditions is illustrated in Figure 5. The corrosion of the transverse cut surface is shown in Figure 6.

![Figure 5. Corrosion on the HB2 bar surface after ageing: a) 180 °C/4h underaged, b) 180 °C/4h + 205 °C/4h two-stage peak-aged, c) 160 °C/4h + 220 °C/4h overaged.](image)
In HB2 drawn bars, IGC was found only in the underaged condition. This intergranular corrosion is not continuous. In the peak-aged and overaged conditions, the bar’s surface only exhibits pitting corrosion with a depth of about 100 µm.

Besides that, corrosion spreads parallel to and beneath the surface, along the bands of coarse cathodic phases. Authors of [9] describe this type of corrosion as ELA (Exfoliation-Like Attack). On the transverse cut surface, corrosion is of the pitting type as well. It is much deeper and, again, more frequent in the near-surface areas. The depth of attack exceeds 700 µm (Figure 6).

3.5 Corrosion tests after aging of specimens of drawn and straightened bars HF

Surface corrosion of selected specimens in variously aged conditions is illustrated in Figure 7. The corrosion of the transverse cut surface is shown in Figure 8.

In specimens in underaged condition, there is deep IGC on the bar’s surface, as well as on the transverse cut surface. In the peak-aged and overaged conditions, the bar surface only exhibits pitting corrosion that spreads perpendicularly to the surface to a depth of more than 300 µm. It is transgranular corrosion, as it penetrates the grains.
On transverse cut surfaces, the least extensive corrosion was found in the peak-aged condition (Fig. 8a). In the slightly-overaged condition, the corrosion is extensive and deep (Fig. 8b). In increasingly overaged specimens, the number and depth of corrosion attack locations decrease (Fig. 8c).

4 Discussion
The main mechanism of IGC is reported to be the formation of microgalvanic cells between cathodic more noble phases and depleted (precipitate-free) zones along grain boundaries. In this case, the key cathodic phase is the Q-phase \((\text{Al}_2\text{Mg}_3\text{Si}_2\text{Cu}_2)\) which precipitates along grain boundaries. As a result, the grain boundary areas become depleted of Cu and other elements. In addition, a thin Cu film forms along grain boundaries and plays the key role in IGC growth and propagation [3, 4, 5, 6]. The entire precipitation process is thermally activated and depends on the diffusion of alloying elements. Its rate is described by Arrhenius equation. With increasing ageing temperature and time, the Q-phase precipitates coarsen and the volume fraction of the Cu film along grain boundaries decreases. Consequently, the susceptibility to IGC is reduced and the material typically exhibits only pitting corrosion.

EN AW-6064 alloy contains a number of other primary cathodic phases (Bi, Pb, alpha-\(\text{Al}_1\alpha(\text{Fe,Mn,Cu,Cr})\text{Si}_2\)). Their arrangement in bands with short distances between phases helps the pitting corrosion to propagate larger depths, most notably beneath the transverse cut surface. In some cases, there were great differences between the corrosion attack on the bar’s surface and on the transverse cut surface.

In the extruded bars (HA1), it was found that with increasing overageing the large-depth IGC changes into shallower pitting corrosion, which is in agreement with findings presented in [3-6]. In the overaged condition, the corrosion penetrations on the transverse cut surface were smaller. Sporadic pitting corrosion with a depth of about 100 \(\mu\text{m}\) was found.

In drawn bars (HB2), the transition from IGC to shallower pitting corrosion was observed as well. Unlike the specimens from bars which had not been drawn, all specimens in this group showed very deep corrosion (more than 700 \(\mu\text{m}\)) on their transverse cut surfaces (Figure 6).

In the drawn and straightened bars (HF), another type of corrosion was observed. In underaged bars, IGC was found on both the bar surface and the transverse cut surface. With ongoing ageing, IGC changes into pitting corrosion which – on the bar surface – propagates perpendicularly to the surface and by transgranular mechanism to a larger depth than pitting corrosion in drawn bars (Figure 7). This corrosion type corresponds to transgranular stress corrosion cracking (SCC) [13]. The difference can be attributed to the variation between internal stresses induced by drawing and straightening. Drawing typically induces tensile stress. Straightening, however, involves alternating bending loads and tensile and compressive stresses which lead to non-uniform residual stress that promotes corrosion propagation perpendicularly to the surface and to a larger depth. The transverse cut surface, unlike HB2 specimens, shows – in some cases – shallow sporadic pitting corrosion (Figure 8a, c).

5 Conclusion
Extruded and drawn bars from EN AW-6064A alloy were used for exploring the impact of thermomechanical treatment on intergranular corrosion (IGC). The effects of forming (drawing and straightening) and artificial ageing were mapped, along with the type of corrosion and corrosion depth on bar surface and its transverse cross-section. The corrosion tests were carried out in accordance with EN ISO 11486 – method B.

The results of the corrosion tests show that thermomechanical treatment affects both the type and depth of corrosion.

The bar surface exhibited three types of corrosion:
- IGC in underaged specimens: typically extensive corrosion with a depth of more than 300 \(\mu\text{m}\).
• Pitting corrosion in more aged and overaged extruded/drawn bars, where the corrosion depth was approximately 100 µm.
• Transgranular pitting corrosion in more aged and overaged bars which had undergone final straightening. Here, the corrosion depth was larger and exceeded 300 µm.

With more intensive ageing and overageing (temperature, time), IGC changed into pitting corrosion in extruded/drawn bars. There was an adverse impact of the post-drawing straightening operation on the resistance to surface corrosion in the bars, evidenced by deep transgranular pitting corrosion. In most cases, the transverse cross-sections exhibited very deep pitting corrosion with depths up to 800 µm which followed the bands of coarse cathodic phases. Exceptions were found in severely overaged bars (extruded or extruded and straightened) which showed sporadic pitting corrosion with depths of approximately 100 µm.

Acknowledgements
This paper was created by project Development of West Bohemian Centre of Materials and Metallurgy No.: LO1412, financed by the MEYS of the Czech Republic.

References
[1] Altenpohl D G 1998 Aluminum: Technology, Applications, and Environment: A Profile of a Modern Metal (Warrendale: Minerals, Metals, and Materials Society).
[2] Hatch J E 1984 Aluminium - Properties and Physical Metallurgy (Ohio: ASM) p 50.
[3] Svenningsen G, Lein J E, Bjorgum A, Nordlien J H, Yu Y D and Nisancioglu K 2006 Effect of low copper content and heat treatment on intergranular corrosion of model AlMgSi alloys Corrosion science 48(1) pp 226–242
[4] Svenningsen G, Larsen M H, Nordlien J H and Nisancioglu K 2006 Effect of high temperature heat treatment on intergranular corrosion of AlMgSi(Cu) model alloy Corrosion science 48(1) pp 258–272.
[5] Svenningsen G, Larsen M H, Walmsley J C, Nordlien J H and Nisancioglu K 2006 Effect of artificial aging on intergranular corrosion of extruded AlMgSi alloy with small Cu content Corrosion science 48(6) pp 1528–1543.
[6] Larsen M H, Walmsley J C, Lunder O, Mathiesen R H and Nisancioglu K 2008 Intergranular Corrosion of Copper-Containing AA6xxx AlMgSi Aluminum J. Electrochem. Soc. 155(11) pp C550-C556.
[7] Guillaumin V and Mankowski G 2000 Influence of Overaging Treatment on Localized Corrosion of Al 6056 Corrosion 56 pp 12-23.
[8] Gallais C, Denquin A, Brechet and Lapasset G 2008 Precipitation microstructures in an AA6056 aluminium alloy after friction stir welding: Characterisation and modelling Mater. Sci. Eng. A496 pp 77–89.
[9] Eckermann F, Suter T, Uggowitzer P J Afseth A and Schmutz P 2008 Investigation of the exfoliation-like attack mechanism in relation to Al–Mg–Si alloy microstructure Corrosion Science 50 (7) pp 2085–2093
[10] Wang Z, Li H, Miao F, Sun W, Fang B, Song R and Zheng Z 2014 Improving the intergranular corrosion resistance of Al–Mg–Si–Cu alloys without strength loss by a two-step aging treatment Mater. Sci. Eng. A590 pp 267-273.
[11] Halap A, Popović M, Radetić T, Vaščić V and Romhanji E 2014 Influence of the thermo-mechanical treatment on the exfoliation and pitting corrosion of an AA5083-type alloy Materiali in tehnologije / Materials and technology 48 pp 479–483
[12] EN ISO 11846:1995. Corrosion of metals and alloys. Determination of resistance to intergranular corrosion of solution heat-treatable aluminium alloys.
[13] ASM Handbook Vol. 13. Corrosion 1987 (Ohio: ASM)