RELEVANCE OF COPPER AND SILICON IN INTERCRYSTALLINE CORROSION OF AA6000-SERIES ALUMINIUM ALLOYS

Magnus Hurlen Larsen and Kemal Nisancioglu
Department of Materials Science and Engineering
Norwegian University of Science and Technology
N-7491 Trondheim, Norway

ABSTRACT: Aluminium 6000-series alloys are normally corrosion resistant. Susceptibility to intergranular (IGC) of alloys with low Cu content may occur, and this is often attributed to excess Si content. In this study we investigate the role of low Cu content and heat treatment on IGC susceptibility of an extruded model alloy containing nominally 0.5% Mg, 0.6% Si, 0.2% Fe, 0.2% Cu and 0.1% Mn. As-extruded material in the T4-temper was resistant to IGC. Underaging introduced significant IGC susceptibility. By aging to the T6 condition, IGC was reduced or eliminated. Overaging introduced susceptibility to pitting. A model alloy of similar composition, but lower (0.02%) Cu content, was not susceptible to IGC in any of these tempers. Detailed transmission electron microscopy of the susceptible specimens revealed the presence of a continuous, few monolayers thick Cu film along the grain boundaries together with discrete precipitates of AlMgSiCu Q-phase. By increasing the aging time, the Cu film became discontinuous, and coarsening of the precipitates, as well as precipitation in the matrix, occurred. These phenomena reduced the IGC susceptibility. The IGC-susceptibility of low Cu-containing 6000-series extrusions is therefore attributed to the formation of the Cu film along the grain boundaries, and depletion of Si in a narrow adjacent zone is a contributing factor. Judicious heat treatment prevents IGC of these materials.

Keywords: Aluminium alloy AA6000, intercrystalline corrosion, microstructure, TEM

Introduction
Al-Mg-Si-(6000series) alloys are medium to high strength alloys with good formability, and they are widely used in architectural and automotive applications. 6000-series aluminium alloys are generally known to be resistant to intergranular corrosion (IGC). However, unfavourable alloying and thermomechanical history may introduce susceptibility to IGC. Excess silicon relative to that needed to form Mg2Si has been claimed to introduce IGC-susceptibility due to the strong cathodic nature of elemental Si [1-3]. Copper additions may form noble grain boundary precipitates with an adjacent Cu-depleted active zone. Svenningsen et al.[3-6] studied the effect of thermomechanical history on the corrosion performance of AlMgSi(Cu)-alloys, and found that slow cooling after extrusion introduced susceptibility to intergranular corrosion. Artificial ageing reduced the IGC-susceptibility. The IGC-susceptibility was related to a nanoscale Cu-rich film along the grain boundaries, along with coarse Cu-containing precipitates at the grain boundaries. The purpose of this work is to contribute to the understanding the relationship between small (0.2%) Cu content, heat treatment and IGC susceptibility by studying the effect of artificial ageing on grain boundary structure and IGC of a water quenched 6000-series model alloy.
Experimental

Two model alloys with similar composition were used. The main difference between the materials was the Cu-content. The compositions are given in table 1.

Table 1. Alloy compositions (wt%)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Si</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Cu</td>
<td>0.52</td>
<td>0.60</td>
<td>0.18</td>
<td>0.21</td>
<td>0.14</td>
<td>Balance</td>
</tr>
<tr>
<td>Low Cu</td>
<td>0.50</td>
<td>0.59</td>
<td>0.02</td>
<td>0.20</td>
<td>0.15</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The materials were extruded to flat profiles in a 8MN laboratory press. Samples were solution heat treated for 30 minutes at 540°C followed by water quenching. Artificial ageing was performed in an oil bath at 185°C for 2500 seconds (underaged), 5 h (T6) and 24 h (overaged) respectively.

An accelerated corrosion test (BS-ISO 11846 method B)[7] was used to determine the susceptibility to IGC. In short, the test involves degreasing, alkaline etching and desmutting in concentrated nitric acid, followed by 24 h immersion in an acidified (1% HCl) salt solution (30 g NaCl/l). TEM samples were prepared by grinding and polishing to ~100µm foil thickness, followed by electropolishing in HNO₃/methanol solution (1:2) at -30°C. The foils were ion beam milled at low angle for 30-60 minutes prior to TEM examination.

Imaging and EDS analysis were performed in a JEOL 2010F FE-TEM operated in the scanning mode.

Results

The low Cu alloy was not susceptible to IGC, regardless of temper. Fig. 1 shows cross sectional micrographs of the Cu-containing alloy after the corrosion test. In the naturally aged condition (T4), the material was severely etched at the surface, leaving a sponge-like structure. The underaged material was highly susceptible to IGC, showing uniform IGC to a depth of more than 500µm over the entire surface. In the peak-aged (T6) and overaged tempers, the material was still slightly susceptible to IGC, but with only localized, shallow attacks.

Figure 1. Cross sectional micrographs showing the high Cu alloy after corrosion test. a) T4, b) underaged and c) T6. The corrosion morphology of the overaged variant was similar to that of T6.

FE-SEM investigation of the materials showed no visible grain boundary precipitation in the case of naturally and underaged tempers, whereas the grain boundaries were decorated with precipitates in the peak-aged and overaged tempers. These precipitates, probably Q-phase (Al₈Mg₈Si₇Cu₂) or a precursor to this phase, were too small for EDS-
analysis in the SEM. Grain boundary precipitation of this phase is documented and discussed in detail elsewhere [4-6].

Figure 2. Electron micrographs of a) underaged and b) overaged materials. The samples were electropolished in order to enhance the contrast.

FE-TEM examination of the T4 material did not reveal any grain boundary precipitation. In the case of the underaged material, scattered precipitates of the order of 10 nm in size, were found at the grain boundaries. Element maps obtained by STEM revealed grain boundary precipitates containing Al, Mg, Si and Cu. In addition, a Cu film was observed along the grain boundary between the precipitates. No enrichment of Mg or Si was found at these sites. These observations were also confirmed by line scans. The line scans could not detect depletion of any elements in the zones adjacent to the grain boundary.
Figure 3. EDS element mapping of a grain boundary in the underaged material, showing the analyzed region and Cu, Si and Mg maps.

The corrosion performance of T6 and overaged materials was similar. The overaged variant was chosen for FE-TEM examination (Fig. 4). Precipitates at the grain boundaries contained Al, Mg, Si and Cu. These precipitates were larger and more numerous than those found in the underaged material.

![Figure 4. EDS element mapping of a grain boundary in the overaged material, showing the analyzed region and Cu, Si and Mg maps.](image_url)

**Discussion**

The naturally aged material was not susceptible to IGC, but formed a porous sponge-like layer at the surface due to etching-type of attack during the corrosion test. This phenomenon is not fully understood. However, it only occurs in the high-Cu material, hence it is believed to be caused as a result of selective corrosion of aluminium, autocatalytically driven by the simultaneous enrichment of solid solution Cu at the surface, which acts as the cathode. No grain boundary precipitation or segregation was found in this temper.

The small precipitates found at the grain boundaries in the susceptible underaged temper are probably a Q-phase or a precursor to this phase, as they consist of Al, Mg, Si and Cu. These precipitates along with the Cu film along the grain boundary is believed to contribute to the cathodic activity as grain boundary attack proceeds. The structure of this film remains unknown, while the present data rule out the presence of Mg and Si in the
film. Moreover, the FE-TEM data did not reveal any depletion of Cu (or other elements) adjacent to the grain boundaries. However, the bulk concentration of Cu (0.18wt%) is so low that it may have been difficult to detect any depletion. Due to the segregation of Cu at the grain boundaries, there is reason to assume solute depletion adjacent to the boundaries, making this area anodic to grain bodies and grain boundaries.

In the peak-aged and overaged materials, the susceptibility to IGC is reduced, but not completely eliminated. The grain boundary film coarsens as a result of ageing, as indicated by Fig. 4, which appears to reduce the susceptibility. However, the Cu-enriched film was still present at some grain boundaries in the overaged material. Extensive precipitation of Q-phase type particles also occurred within the grain bodies. This process will lower the Cu-content in solid solution in the grain bodies and thus even out the potential difference between the grain boundary areas and bulk material.

Conclusions
The alloy with low Cu-content (0.02wt%) did not exhibit intergranular corrosion despite the excess Si compared to the Mg2Si stoichiometry. The high-Cu material was susceptible to intergranular corrosion in the underaged temper. This is attributed to a Cu-enriched film at the grain boundaries, providing the cathodic sites. The adjacent zone, which must be depleted in Cu, is active compared to the grain bodies and grain boundaries and is therefore susceptible to knife line IGC. Upon further artificial ageing, the grain boundary precipitates grow in number and size as a result of further precipitation and coarsening of the grain boundary film. This, combined with matrix precipitation, reduces the susceptibility to IGC.

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References