



## General aspects related to the corrosion of 6xxx series aluminium alloys: Exploring the influence of Mg/Si ratio and Cu

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### ABSTRACT

Specially prepared 6xxx series aluminium alloys (Al–Mg–Si) with different Mg/Si ratios and Cu contents were investigated in the naturally aged, under-aged, peak-aged and over-aged conditions. Potentiodynamic polarisation and immersion testing in 0.1 M NaCl were used to investigate the corrosion behaviour of such alloys in a general sense. Results reveal a significant dependence of the corrosion rate and morphology on the ageing conditions and solute content. Whilst contributing to broader understanding of 6xxx alloy corrosion, we note that corrosion rate is lowest in the naturally aged condition and is principally influenced by Cu and subsequently by the Mg/Si ratio.

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### 1. Introduction

Al–Mg–Si (6xxx series) alloys are generally considered to have good corrosion resistance compared to Cu or Zn rich high strength Al-alloys [1]. 6xxx series alloys represent the medium strength class of Al-alloys, as they can respond to age-hardening via Mg<sub>2</sub>Si precipitation, making them stronger than 5xxx Al–Mg solid solution alloys, but not as strong as 2xxx or 7xxx alloys. In order to obtain an optimal combination of mechanical properties, a small amount of Cu or a large excess of Si compared to the stoichiometric Mg/Si ratio corresponding to the Mg<sub>2</sub>Si phase is often used in 6xxx alloys [2,3]. This can result in an increased susceptibility to localised corrosion such as pitting and intergranular corrosion (IGC) [4,5]. The Mg<sub>2</sub>Si phase has been electrochemically characterised in isolation previously [6,7], and is seen to be ‘active’ compared to the Al-alloy matrix. In neutral dilute chloride electrolytes, Mg<sub>2</sub>Si presents an open circuit potential of  $\sim -1.2$  V<sub>SCE</sub>. Furthermore, Mg<sub>2</sub>Si has been noted to undergo a dealloying form of self-dissolution [7–9].

In a series of papers, Svenningsen et al. [10–13] presented a comprehensive study of factors affecting IGC susceptibility of 6xxx series alloy extrusions, containing nominally 0.55 Mg, 0.60 Si and about 0.02 or 0.17 Cu (in wt%). Their results showed that the alloys with lower Cu were essentially resistant to IGC, while the alloys with higher Cu, which were air cooled after extrusion, exhibited significant IGC. However, the IGC susceptibility was re-

duced, and finally eliminated, by artificial ageing, although over-ageing introduced a pitting susceptibility.

In excess Si alloys, in addition to the  $\beta$ -phase (Mg<sub>2</sub>Si) and its precursors, pure Si may precipitate [14]. These Si particles have a tendency to segregate at the grain boundaries and thereby posited to promote IGC [15]. However, when in contact with water, Si precipitates will be covered by an insulating layer of SiO<sub>2</sub>, and are therefore not effective cathodes [12]. A recent paper by Fleming and co-workers shows the complexity associated with localised corrosion arising from Mg<sub>2</sub>Si, eutectic forms of Si at grain boundaries, and variant phases that can form during brazing operations in Cu-containing 6xxx alloys [16]. The study by Fleming indicated that excess Si, and the presence of Cu, affected corrosion characteristics; which the present work seeks to contribute to by the investigation of unique alloys with carefully prepared alloy chemistries.

Thermal treatments such as cooling rate and ageing conditions were also reported to be important in terms of the corrosion susceptibility. El-Menshawey et al. [17] reported that peak aged specimens of AA6061 showed a maximum susceptibility to IGC, while pitting was the dominant corrosion mode for the over-aged tempers. As-solution treated specimens exhibited uniform corrosion and showed the highest resistance to pitting or IGC.

In order to abridge the information in the literature, Table 1 summarises some findings from published works related to the corrosion behaviour of 6xxx series alloys. The different experimental conditions such as alloy composition and heat treatment parameters make a comparative analysis complicated. As seen from Table 1, although localised corrosion phenomena in 6xxx alloys is strongly affected by the chemistry, dimension and distribution of the intermetallic particles and precipitates, the underlying

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**Table 1**  
Summary of corrosion behaviour of 6xxx series alloys as reported in the literature.

Alloys (Composition in wt%)	Experimental Conditions	Corrosion Trends	Corrosion Mechanisms
Al–1.0Si–0.4Mg	550 °C/1 h (ST) + WQ + aged at 170 °C	–	Precipitation of Mg <sub>2</sub> Si at the grain boundary favours IGC attack, and Si particles promote IGC [15]
Al–0.92Si–0.86Mg–0.87Cu	550 °C (ST) + air quenched + aged at 175 °C for 8 h (T6)	–	Si and Cu depleted zones along grain boundaries are dissolved preferential as anodic phases [21]
Al–0.54Si–1.03Mg–0.33Cu	520 °C extruded + WQ + aged at 175 °C/8 h	–	IGC was caused by the dissolution of the precipitate-free zones (PFZs) [22]
Al–0.93Si–0.57Mg, and Al–0.60Si–0.52Mg–0.12Cu	557–569 °C extruded + WQ (or air cooling) + aged at 185 °C/5 h	Air-cooling resulted in most corrosion, but ageing decreased corrosion. WQ gave good corrosion resistance, but ageing made it worse (esp. UA)	The Cu-containing alloy was susceptible to IGC, depending on its thermal history. Precipitation of the Cu-rich Q-phase along the grain boundaries was the most probable cause of IGC [10]
Al–1.0Si–0.5Mg–(0.03–0.80)Cu, and Al–1.0Si–0.8Mg–(0.03–0.80)Cu	560 °C (ST) + WQ + pre-ageing (or none) + aged for 20 min at 175 °C (or 185 °C) + WQ	IGC increased with Cu	IGC was caused by micro-galvanic coupling between the cathodic Q phase precipitates and the aluminium matrix adjacent to the particles [4]
Al–0.59Si–0.50Mg–0.02Cu, and Al–0.60Si–0.52Mg–0.18Cu	540 °C/30 min(ST) + WQ + aged at 185 °C	UA resulted in most corrosion	The Cu-containing alloy was susceptible to IGC, and IGC was due to micro-galvanic coupling between the noble Cu film and the adjacent solute-depleted active zone [5]
Al–1.31Si–0.40Mg Al–0.60Si–0.52Mg–0.18Cu	540 °C/30 min (ST) + WQ (or air cooled) + store 4 h at room + aged at 185 °C	UA resulted in most corrosion	The Cu-containing alloy was more susceptible to IGC than the Cu-free alloy. IGC was caused by micro-galvanic coupling between the cathodic Cu-rich film and solute-depleted active zone [23]
Al–0.28Si–0.63Mg, and Al–0.88Si–0.63Mg	Solution treatment + WQ + aged at 175 °C for 1 h	Mg/Si ratio less than 1.73 resulted in IGC	The Si particles accelerate the preferential dissolution of Mg in Mg <sub>2</sub> Si, expediting the polarity transformation between Mg <sub>2</sub> Si and the PFZ [24]
Al–0.6Si–0.85Mg–0.22Cu	550 °C/1 h(ST) + WQ + aged at different temperatures (225 °C, 185 °C and 140 °C)	PA resulted in most corrosion	Peak-ageing treatment ennobled $E_{corr}$ , increased the cathodic current density and $i_{corr}$ , and shortened the passive region [17]
Al–0.5Si–0.6Mg	T6	–	Mg <sub>2</sub> Si was anodic to Al alloys in the acidic and neutral pH, but cathodic in alkaline Conditions [7].

ST: solution treatment; WQ: water quenching; UA: under-aged; PA: peak-aged.

mechanisms are not adequately explained. This may be rationalised on the basis that microstructural investigations in such alloys are rather complex. The nominal precipitate that can form in the range of compositions studied is Mg<sub>2</sub>Si (with the potential for some pure Si in the case of excessive Si additions), and the Mg<sub>2</sub>Si size range is very fine (<20 nm) following heat treatments typical of paint baking [18–20]. The determination of precipitate characteristics in Al–Mg–Si alloys is aided by atom probe tomography, as shown by Rometsch et al. [20]. In addition to Mg<sub>2</sub>Si, for compositions rich in Cu (from approx.>0.8 wt% Cu), it is reported that Q phase, Al<sub>5</sub>Cu<sub>2</sub>Mg<sub>8</sub>Si<sub>6</sub>, may also develop [3,14,19].

In this work, the corrosion behaviour of a series of 6xxx alloys with different Cu contents and different Mg/Si ratios was investigated at different ageing conditions by means of electrochemical corrosion testing and immersion testing. The purpose of this work is to elucidate the individual and combined effects of Cu, Mg, Si and heat treatment on the corrosion behaviour of the alloys in a first order sense; allowing a platform for more comprehensive understanding of the corrosion of 6xxx alloys which is comparatively much less reported than for other Al-alloy classes.

## 2. Experimental procedure

### 2.1. Materials

The chemical compositions of nine 6xxx series alloys investigated in this work are given in Table 2. The alloy chemistry was independently determined using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP–AES). Alloys were supplied by

**Table 2**  
Chemical compositions of the alloys tested in this work, compositions in wt.%.

Alloy	Si	Mg	Cu	Fe	Mn	Al
A	1.25	0.42	0.001	0.08	0.13	Bal
B	1.26	0.37	0.30	0.09	0.13	Bal
C	1.05	0.53	0.89	0.13	0.17	Bal
D	0.92	0.80	0.001	0.08	0.12	Bal
E	0.91	0.71	0.35	0.08	0.13	Bal
F	0.90	0.74	0.84	0.08	0.14	Bal
G	0.52	1.14	0.001	0.07	0.13	Bal
H	0.48	1.02	0.32	0.09	0.13	Bal
I	0.47	1.05	0.83	0.11	0.20	Bal

Chalco, and were conventionally cast in air at the Suzhou Institute of Nonferrous Metals Research (Suzhou, PRC). Castings were homogenised, hot rolled, and subsequently cold rolled to 1.0 mm thick sheets. The solution treatment and aging was carried out at Monash University.

These nine alloys (Table 2) have a similar total Mg + Si content. Alloys A, B and C have a large excess of Si; alloys D, E and F have a small excess of Si; whilst alloys G, H and I are excess Mg alloys. Alloys A, D and G are essentially Cu-free alloys, and alloys B, E and H contain about 0.30–0.35 wt% Cu, while alloys C, F and I contain about 0.83–0.89 wt% Cu. This combination makes for a comprehensive matrix to be tested.

### 2.2. Heat treatment procedures

All samples were given the same solution heat treatment of 0.5 h at 550 °C in a salt bath, followed by water quenching to room

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