Anti-Corrosion Methods and Materials

Effect of Cu content on the corrosion of Al-Si eutectic alloys in acidic solutions

Sibel Zor
Chemistry Department, Science-Literature Faculty, Kocaeli University, Kocaeli, Turkey

Muzaffer Zeren
Engineering Department, Engineering Faculty, Metallurgical and Materials, Kocaeli University, Kocaeli, Turkey

Hatice Ozkazanc
Chemistry Department, Science-Literature Faculty, Kocaeli University, Kocaeli, Turkey

Erdem Karakulak
Engineering Department, Engineering Faculty, Metallurgical and Materials, Kocaeli University, Kocaeli, Turkey
Effect of Cu content on the corrosion of Al-Si eutectic alloys in acidic solutions

Sibel Zor
Chemistry Department, Science-Literature Faculty, Kocaeli University, Kocaeli, Turkey

Musafer Zeren
Engineering Department, Engineering Faculty, Metallurgical and Materials, Kocaeli University, Kocaeli, Turkey

Hatice Ozkazanc
Chemistry Department, Science-Literature Faculty, Kocaeli University, Kocaeli, Turkey, and

Erden Karakulak
Engineering Department, Engineering Faculty, Metallurgical and Materials, Kocaeli University, Kocaeli, Turkey

Abstract
Purpose – The purpose of this paper is to understand corrosion behavior of different Cu-containing Al-Si-x% Cu alloys (x: 1 wt% Cu, 2 wt% Cu, 3 wt% Cu, 4 wt% Cu, and 5 wt% Cu) in 0.1 M HCl and 0.1 M H_2SO_4.
Design/methodology/approach – Potentiodynamic, chronocamperometric and impedance measurements were applied to specimens to obtain their electrochemical characteristics. For the long-term analyses, hydrogen evolution with immersion time (V-4) was measured. The corroded surfaces of the alloys were investigated using scanning electron microscopy (SEM) to understand the corrosion mechanism.
Findings – All experimental investigations showed that the corrosion resistance of alloys increased with increasing Cu content in the alloys.
Research limitations/implications – Cu-containing aluminum alloys are age-hardenable alloys. The corrosion behaviour of these alloys can be changed by heat treatment. Corrosion test results for the heat treated and aged alloys will be discussed in another study.
Originality/value – Al-Si-Cu alloys are widely used in the automobile industry and the corrosion behaviour of these alloys has a great importance on the service life of these materials. Understanding the effect of copper and the corrosion mechanism of these alloys will be helpful in predicting and prolonging the service life of these materials.

Keywords Alloys, Corrosion, Acids, Electrochemistry, Physical properties of materials

Paper type Research paper

1. Introduction
Aluminum and its alloys are important materials for use in many applications such as automobiles, aviation, household appliances, containers, and electronic devices (Bakos and Szabó, 2008; Amin et al., 2008; Yang, 1994; Capuano and Davenport, 1971), owing to its many favorable characteristics, which include good electrical and thermal conductivities, low density, high ductility, and good corrosion resistance. The corrosion resistance of aluminum arises from the presence of a stable oxide film on its surface.

Although pure Al does not have sufficient strength to be used as a heavy-duty material for large structures, high-strength Al alloys can be produced by addition of appropriate alloying elements such as Cu, Mg, and Zn and by suitable heat treatment procedures (Andretta et al., 2003; Cabot et al., 1995).

The primary advantage of aluminum alloys in general is a relatively high strength to weight ratio (Osório et al., 2007). Al-Si-based alloys are the most used non-ferrous alloys because of their low density, high corrosion resistance, ease of casting, low-thermal expansion coefficient, and a wide range of mechanical properties (Zeren and Karakulak, 2008).

These properties allow Al-Si alloys to replace some ferrous alloys in automotive, transportation, acroplane, and defense industries (Saheb et al., 2001; Liu et al., 2004). However, in some cases the strength increase produced by the silicon addition is not sufficient. In this situation, a third alloying element is necessary. In general, Cu or Mg is chosen as the supplementary alloying element because of their capability to allow age hardening of the alloys. Copper is added to aluminum alloys to increase their tensile strength, hardness, fatigue and creep resistance, and to improve machinability. In specific compositions and metallurgical conditions and service environments, copper can cause stress corrosion susceptibility (Osório et al., 2007; Stefanescu, 1988; Liu et al., 2005). This is because of the presence of Cu-rich precipitates at grain boundaries. The precipitates reduce the intergranular corrosion (IGC) resistance of the material (Svendingsen et al., 2006a, b, c). This study shows that while IGC resistance may decrease, the general corrosion resistance of the alloys may increase with Cu addition.

To understand this behavior, different Cu-containing (1, 2, 3, 4, and 5 percent) Al-Si alloys were tested using electrochemical methods in 0.1 M HCl and 0.1 M H_2SO_4 solutions. The
Effect of Cu content on the corrosion of Al-Si eutectic alloys
Sibel Zengin, Muzaffer Zeren, Hatice Oztascan and Erkem Karakulak

Corroded surfaces of alloys were examined after exposure using an scanning electron microscopy (SEM) to understand better the corrosion mechanisms.

2. Materials and methods

2.1 Materials
The Al-Si-x% Cu alloys were utilized by melting Al-Si eutectic alloys (containing ~11.7 percent Si) and adding Cu into the melt. The melting operation was carried out in an electric resistance furnace and the alloys were cast into a permanent steel mold with dimensions of 3 x 5 x 10 cm. No degassing treatment was used before the casting operation. After solidification of alloys, suitable specimens were cut and used for the experiments. In the age-hardenable Al-Cu alloys before solution heat treatment the Cu exists at grain boundaries, whereas after aging heat treatment the Cu-containing phases are dispersed in the grains and increase strength of the material. The existence of copper as precipitates at grain boundaries or dispersed in the grains affects the corrosion behavior quite differently (Keddam et al., 1997). In the present study, the specimens were investigated in the as-cast condition without heat treatment.

2.2 Microstructure
Samples from the castings were prepared by mechanical grinding. Finish polishing was carried out using 3 μm diamond particles. Keller's reagent was used (1% HF + 1.5% HCl + 2.5% HNO₃ + 95% H₂O) to reveal the microstructures of polished specimens. An optical microscope was used during the microstructural analysis. The microstructural investigation shows that increasing Cu content in the alloys caused an increase in the Cu-containing intermetallic phases. These phases were mainly evident at the grain boundaries. Figure 1 shows microstructures of different Cu-containing alloys. In Figure 1(a) the microstructure of the 2 percent Cu-containing alloy is shown. The white areas are α-Al. The needle shaped grey phases are silicon and the brown phases are copper-containing phases (b-phase). The b-phase in Al-Cu alloys is generally known as Al₂Cu (Gao et al., 2006). Figure 1(b) shows microstructure of 5 percent Cu-containing alloy. The volume fraction of the Cu-containing phase increased with increasing copper content.

To understand the corrosion mechanism, samples were exposed in 0.1 M HCl and 0.1 M H₂SO₄ solutions for 120 h and then were examined using a Jeol 6060 type SEM. The results of these investigations will be given in results and discussion sections.

2.3 Electrochemical measurements
Al-Si, Al-Si-x% Cu (x = 1, 2, 3, 4, 5 wt%) alloys were used as the working electrode. The investigated electrodes were cut as cylindrical rods and a copper wire was welded on to provide an electrical connection. The exposed area to the corrosive solution was 0.785 cm². Prior to each measurement, the working electrodes (samples) were further ground to a 1,000 grit SiC finish, followed by polishing with 3 μm diamond. The electrodes then were rinsed with acetone and distilled water, and finally they were immersed in the electrolytic cell. Pt wire and a saturated calomel electrode were used as auxiliary and reference electrodes, respectively. The reference electrode was connected to a Luggin capillary to minimize IR drop. All solutions were prepared using distilled water.

A computer-controlled Gamry Reference 600 potentiostatic/galvanostat was used for the electrochemical measurements. Electrochemical measurements were carried out in 0.1 M HCl and 0.1 M H₂SO₄ solutions at room conditions. The polarization curves were obtained potentiodynamically over the range -1.0 to +1.0 V at a scan rate of 20 mV s⁻¹. Electrochemical impedance spectroscopy measurements were made over the frequency range 100-1000 kHz using a sinusoidal a.c. signal of 7 mV at Ecorr. The chronocapacitometric measurements were carried out at a fixed potential of -1.0 V.

For hydrogen gas evolution measurements, a burette was filled with 0.1 M HCl solution and was up-turned over the working electrode. The initial air volume available in the burette was recorded and the volume of H₂ gas evolved from the corrosion reaction was monitored by the volume change as a function of time.
3. Results

3.1 Hardness tests
The hardness measurements of the as-cast alloys were obtained by using a Future-Tech FV-700 model Vickers hardness tester. Each reported value was an average of five measurements. All hardness measurements were made using 3 kg (HV3) load and 10 s dwell time at room temperature. Figure 2 shows effect of Cu on the hardness of the alloys.

3.2 SEM examination
SEM micrographs of the different Cu-containing alloys after immersion in 0.1 M HCl and 0.1 M H₂SO₄ for 120 h are shown in Figures 3 and 4, respectively.

In both solutions, the corrosion resistance of the alloys was affected by the microstructural properties of the alloys. The microstructure of the alloys comprised Al solid solution (α-phase), silicon needles and Cu-containing intermetallics (β-phase). The intermetallic phases were more noble than the Al solid solution phase and this can cause microcells of galvanic corrosion when the two phases coexist in a microstructure.

3.3 Potentiodynamic results
Figures 5 and 6 show the potentiodynamic polarization curves of different Cu-containing alloys in 0.1 M HCl and 0.1 M H₂SO₄ solutions, respectively. Electrochemical parameters, namely corrosion potential and corrosion current, were obtained from the polarization curves by Tafel extrapolation and are given in Table I.

3.4 Impedance measurements
Suggested equivalent circuit model and Nyquist curves for alloys with different Cu content in 0.1 M HCl and 0.1 M H₂SO₄ solutions are shown in Figures 7-9, respectively, (Rc: solution resistance, Rp: polarization resistance, double-layer capacitance (Cdl)). In Nyquist diagrams, the imaginary component of the impedance (Z”) against real part (Z’) is obtained in the form of a capacitive-resistive semicircle for each sample. In both of the two solutions, the radius of the semicircles increased with increasing Cu content. Inductive loops were observed in Nyquist diagrams for the tests carried out in the acidic solutions. It has been suggested that the reason for these inductive loops is anion adsorption at the metal-solution interface (Svenningsen et al., 2006a, b, c; Singh et al., 2009). Impedance parameters (Rc, Rp, and Cdl)

Figure 2: Effect of Cu content on hardness of Al-Si alloys

![Effect of Cu content on hardness of Al-Si alloys](image)

Anti-Corrosion Methods and Materials
Volume 57 · Number 4 · 2010 · 185–191

Figure 3 SEM images of specimens after 120 h immersion in 0.1 M HCl solution

(a)

(b)

Notes: (a) Al-Si + 3% Cu; (b) Al-Si + 5% Cu

generated from the Nyquist curves, using a suggested equivalent circuit model, are given in Table II.

3.5 Chronoamperometric measurements
Figures 10 and 11 show the results of chronoamperometric measurements for different Cu-containing Al-Si alloys in 0.1 M HCl and 0.1 M H₂SO₄, respectively. As can be seen from Figure 10, the value of current decreased from 135 to 118 mA after 3,600 s for the alloys. This value was estimated to be 89 mA for Al-Si-1% Cu and 10 mA for Al-Si-5% Cu alloys.

A similar behavior was observed in the H₂SO₄ solution (Figure 11). After 3,600 s, current values in 0.1 M H₂SO₄ solution are recorded as follows: 1.3 mA for Al-Si alloy, 1.2 mA for Al-Si-1% Cu alloy, 0.7 mA for Al-Si-3% Cu alloy and 0.2 mA for Al-Si-5% alloy.

3.6 Hydrogen evolution
Figure 12 shows the hydrogen evolution caused by the corrosion of Al-Si, Al-Si-1% Cu and Al-Si-5% Cu alloys in 0.1 M HCl solution. The volume of evolved hydrogen decreased with increasing time. After 120 h of immersion in 0.1 M HCl solution, 475 ml H₂ was reported for Al-Si alloy whereas 145 ml was evolved with the Al-Si + 1% Cu alloy and only 43 ml was evolved for the Al-Si + 5% Cu alloy.
Effect of Cu content on the corrosion of Al-Si eutectic alloys

Sikel Zor, Mustafier Zoren, Hatice Ozkazanc and Erdem Karabuduk

Figure 4 SEM images of specimens after 120 h immersion in 0.1 M \( \text{H}_2\text{SO}_4 \) solution

![SEM images of specimens](image)

Notes: (a) Al-Si + 2% Cu; (b) Al-Si + 4% Cu

Figure 5 Polarization curves of Al-Si + xCu (x: 1 wt% Cu, 2 wt% Cu, 3 wt% Cu, 4 wt% Cu, and 5 wt% Cu) in HCl solution

![Polarization curves](image)

Table 1 Electrochemical parameters obtained from polarization curves

<table>
<thead>
<tr>
<th></th>
<th>0.1 M HCl</th>
<th>0.1 M ( \text{H}_2\text{SO}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{I}_{\text{cor}} ) (( \mu \text{A/cm}^2 ))</td>
<td>( E_{\text{cor}} ) (mV)</td>
</tr>
<tr>
<td>Al-Si</td>
<td>1,415</td>
<td>−682.3</td>
</tr>
<tr>
<td>Al-Si + 1% Cu</td>
<td>1,674</td>
<td>−659.2</td>
</tr>
<tr>
<td>Al-Si + 2% Cu</td>
<td>192.5</td>
<td>−993.4</td>
</tr>
<tr>
<td>Al-Si + 3% Cu</td>
<td>148.9</td>
<td>−886.5</td>
</tr>
<tr>
<td>Al-Si + 4% Cu</td>
<td>88.95</td>
<td>−946.5</td>
</tr>
<tr>
<td>Al-Si + 5% Cu</td>
<td>74.72</td>
<td>−955.6</td>
</tr>
</tbody>
</table>

Figure 6 Polarization curves of Al-Si + xCu (x: 1 wt% Cu, 2 wt% Cu, 3 wt% Cu, 4 wt% Cu, and 5 wt% Cu) in \( \text{H}_2\text{SO}_4 \) solution

![Polarization curves](image)

Figure 7 Suggested equivalent circuit model for Al-Si + xCu impedance curves

![Equivalent circuit model](image)

Figure 8 Impedance of Al-Si + xCu (x: 1 wt% Cu, 2 wt% Cu, 3 wt% Cu, 4 wt% Cu, and 5 wt% Cu) in HCl solution

![Impedance curves](image)

A similar experiment was carried out in 0.1 M \( \text{H}_2\text{SO}_4 \) solution. However, after 120 h of immersion a very much smaller volume of hydrogen (2-25 ml) had been evolved than had been the case in the 0.1 M HCl solution.
4. Discussion

As shown in Figure 2, the hardness values of alloys increased with increasing Cu content. Addition of Cu to Al-Si alloys increases the hardness and strength of the alloys.

In the SEM observations, it was observed that the microstructure of the alloys consisted of θ-phase surrounded by eutectic α-aluminum phase. The α-Al phase is more anodic then is the θ-phase and corrosion occurs on the α-phase (Figures 3 and 4). θ-phase is precipitated at grain boundaries and acts like a corrosion barrier, limiting the degree of corrosion in the grains. While θ-phase intermetallics at the grain boundaries seem not to be corroded; corrosion occurs inside the Al-rich α grains (Figures 3 and 4). Corrosion occurs in the form of pitting when Cl− ions exist in the solution, or if the solution is acidic.

As can be seen from the potentiodynamic polarization curves shown in Figure 5, cathodic current density decreased with increasing Cu content in the Al-Si + xCu alloys, which is related to the reduction in the cathodic reaction rate. θ intermetallic phases in the Al-Si + x% Cu alloys reduce the electron transportation rate, which is required for the cathodic reaction (2H + 2e − H₂). The corrosion potential of alloys moves to more negative values, and corrosion current density is reduced, with increasing Cu content (Table I). For Al-Si + 1% Cu alloy, corrosion current density is 1,674 μA/cm² but increasing the Cu content to 5 percent decreased this value to 74.72 μA/cm², which is equivalent to a 95.5 percent reduction in the corrosion current density (Table I). The anodic and
Effect of Cu content on the corrosion of Al-Si eutectic alloys

Anti-Corrosion Methods and Materials

Sibel Zor, Muzaffer Zeren, Hatice Ozkazanc and Erdem Karakulak

Sibel Zor, Muzaffer Zeren, Hatice Ozkazanc and Erdem Karakulak

cathodic current densities of Al-Si + x% Cu alloys in 0.1 M H₂SO₄ decreased with increasing Cu content (Figure 6), which meant that the anodic and cathodic reaction rates reduced. The corrosion potential moved to more noble values when the Cu content in the alloys was higher (Table I).

In Al-Si alloys, silicon reduces local cathodic reaction rates. Cu addition to these alloys leads to the precipitation of AlCu₂ intermetallic phases, which act as the cathode of the local galvanic cell. AlCu₂ acts as the cathode because it is more noble than the matrix and the oxide film on these phases is thinner so there is a smaller resistance for electrons to flow through these phases. Pitting corrosion and the dissolution of metal (Al → Al⁺³ + 3e⁻) starts on the aluminum matrix surrounding these phases.

Impedance measurements showed that in both solutions, increasing Cu in the alloys increased polarization resistance. For the Al-Si alloy without Cu addition, the Rₑ value in 0.1 M HCl solution was 210, and this value is increased to 1,027 with addition of 5 percent Cu to the alloy. A similar increase was reported for 0.1 M H₂SO₄ solution, where the Rₑ value increased from 341.8 to 1,886 with the addition of 5 percent Cu. These increases in the polarization resistance show the increase in the corrosion resistance of the alloys with Cu addition. The increase in the Rₑ value in H₂SO₄ solution was greater than in the HCl solution, which means that the Cu addition was more effective in H₂SO₄ solution in reducing the corrosion rate (Table II). It can also be observed that the Al-Si + 5% Cu alloy exhibited better corrosion resistance than did the other alloys. It seems that the more noble electrochemical behavior of this alloy essentially could be explained by the higher volume fraction of Cu-containing intermetallic phases.

For chronoamperometric measurements in both HCl and H₂SO₄ solutions, alloys with Cu have lower double-layer capacitance (Cₛ) values than did the Al-Si alloy (Table II). The increase in polarization resistance and decrease in double-layer capacitance was indicative of the reduction in the active corrosive area with copper addition to Al-Si alloys.

In both solutions, with increasing copper content the measured current value decreased. The decrease in current was a result of the decrease in the number of Al atoms which dissolve and go to solution as Al⁺³ ions. This is manifested as a decrease in the corrosion rate.

The lowering of the corrosion current flow values of the alloys was more efficient in 0.1 M H₂SO₄ solution. The reason for this behavior could be the presence of Cl⁻ ions in the HCl. It is well known that existence of Cl⁻ ions in solution causes higher corrosion rates on aluminum alloys (Zhang et al., 2007).

H₂ evolution tests showed that with increasing Cu content in the alloys, hydrogen evolution decreased, which also is indicative of a decrease in the corrosion rate, because hydrogen evolution is related to the dissolution of aluminum. Another finding from the hydrogen evolution tests was that corrosion in HCl solution occurred more rapidly than was the case in H₂SO₄ solution, which supported the findings from the chronoamperometric measurements.

5. Conclusions

- Additions of copper to Al-Si eutectic alloys cause the precipitation of Cu-rich (β-phase) particles in the grain boundaries. With increasing Cu content, the volume fraction of the β-phase particles increases.
- The electrochemical parameters obtained from polarization curves showed that with increasing Cu content, corrosion current density decreased in both solutions.
- The magnitude of the Rₑ (polarization resistance) value, as a impedance parameter, increased with increasing Cu content. Rₑ-values for 0.1 M H₂SO₄ solution were higher than were the values obtained in 0.1M HCl solution.
- From the chronoamperometric tests, it was reported that when the Cu content was higher in the alloy, the current was decreased. The degree of current reduction was greater in the H₂SO₄ solution.
- H₂ evolution tests showed that increasing the Cu content in the alloys caused a reduction in the amount of H₂ gas evolved.
- All the test results showed that the corrosion resistance of Al-Si alloys alloys was increased by the addition of 1-5 percent Cu. The effect of copper was more effective in H₂SO₄ solution then HCl solution. However, during SEM examinations of the corroded surfaces of specimens it was reported that an increase in the Cu content was associated with a concurrent increase in the rate of IGC. This suggests that corrosion will occur more locally at grain boundaries, whereas the general rate of corrosion may be decreased when Cu is added to Al-Si alloys.

References


Effect of Cu content on the corrosion of Al-Si eutectic alloys

Sibel Zor, Mazaffar Zeren, Hatice Ozkazanc and Erdem Karakulak


Anti-Corrosion Methods and Materials

Volume 57 · Number 4 · 2010 · 185–191


Corresponding author

Erdem Karakulak can be contacted at: erdemkarakulak@kocaeli.edu.tr

To purchase reprints of this article please e-mail: reprints@emeraldinsight.com
Or visit our web site for further details: www.emeraldinsight.com/reprints

191