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The effect of 4 wt.% Cu addition on the electrochemical corrosion behavior of automotive engine Al-6Si-0.5Mg alloy

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The purpose of this paper was to investigate the effect of 4 wt.% Cu addition on the electrochemical corrosion behavior of Al-6Si-0.5Mg alloy in NaCl solution. The corrosion of thermally treated samples was characterized by electrochemical techniques. On the whole, the electrochemical test showed that Cu addition increases the corrosion rate of the alloy. The magnitude of the noble shift in the open circuit potential (OCP), corrosion potential (E_{corr}) and pitting corrosion potential (E_{pit}) increased with the addition of 4 wt.% Cu to the Al-6Si-0.5Mg alloy.

Al-6Si-0.5Mg-4Cu alloy / Electrochemical test / SEM

Introduction

Aluminum and its alloys are considered to be highly corrosion resistant under the majority of service conditions. When an aluminum surface is exposed to atmosphere, a thin invisible oxide (Al_2O_3) skin forms, which protects the metal toward corrosion in many environments [1]. This film protects the metal from further oxidation and, unless the coating is destroyed, the material remains fully protected against corrosion. The composition of the alloy and its thermal treatment are important for the susceptibility of the alloy to corrosion [2-5].

Over the years, a number of studies have been carried out to assess the effect of the Cu content and the distribution of intermetallic particles of secondary phases on the corrosion behavior of Al-alloys. The Cu distribution in the microstructure affects the susceptibility to localized corrosion. Pitting corrosion usually occurs in the Al-matrix near Cu-containing intermetallic particles, owing to galvanic interaction of the latter with the Al-matrix. Intergranular corrosion (IGC) is generally believed to be associated with Cu-containing grain boundary precipitates and the precipitate free zone (PFZ) along the grain boundaries [6-8]. In heat treated Al–Si–Mg(–Cu) alloys, it was found that the susceptibility to localized corrosion (pitting and/or intergranular (IGC)) and the extent of the attack are mainly controlled by the type, amount and distribution of the precipitates that form in the alloy during any thermal or thermomechanical treatments performed during manufacturing processes [9-13].

Depending on the composition of the alloy and parameters of the heat treatment process, these precipitates form at the grain boundaries, or in the bulk as well as at the grain boundaries. As indicated by several authors, the precipitates formed by heat treatment in Al–Si–Mg alloys containing Cu are the θ-phase (Al_2Cu), Q-phase ($Al_4Mg_8Si_7Cu_2$), β-phase (Mg_2Si), and free Si, if the Si content in the alloy exceeds the Mg_2Si stoichiometry [14-17].

Copper is mainly added to increase the strength; at low temperature by heat treatment, at higher temperatures through the formation of compounds with iron, manganese, nickel, *etc.* As for wrought alloys, copper is the most deleterious alloying element regarding general corrosion of cast alloys. Alloys such as 356.0, 513.0, and 514.0, which do not have copper as an alloying element, have high resistance to general corrosion, comparable to that of non heat-treated wrought alloys. In other alloys the resistance becomes progressively less the higher the copper content [18,19]. Copper-bearing alloys tend to pit severely in the annealed condition and when age-hardened they may be susceptible to intergranular or stress corrosion. Cu also shifts the open-circuit potential in the positive or noble direction [20], however, the upward shift does not imply that the alloy is less susceptible to corrosion. The shift in the noble direction occurs as a result of addition of elements more noble than Al. The presence of noble elements, especially if present as precipitated constituents, actually leads to an increase in the corrosion susceptibility of the alloy, as a result of the formation of a localized galvanic couple [21,22].

The present study is an attempt to understand the effect of 4 wt.% Cu on the electrochemical corrosion behavior of an Al-6Si-0.5Mg alloy in 0.1M NaCl solution by examining the corroded surfaces by scanning electron microscopy (SEM). The Al-6Si-0.5Mg alloy is used in automotive engines.

Experimental setup and procedures

Materials and processing

The alloys were prepared by melting Al-7Si-0.3Mg (A356) alloys and adding Cu into the melt. The melting operation was carried out in a clay-graphite crucible in a gas-fired furnace and the alloys were cast into a permanent steel mould. After solidification of the alloys, rectangular samples (30 mm × 10 mm × 5 mm) were cut. The samples were homogenized (500°C for 24 h) and solutionized (540°C for 2 h), and finally artificially aged (225°C for 1 h). After the heat treatment, the samples were prepared for metallographic examination and finally subjected to electrochemical tests. Deionized water and analytical reagent grade sodium chloride (NaCl) were used for the preparation of a 0.1M solution. All measurements were carried out at room temperature.

Electrochemical tests

A computer-controlled Gamry Framework TM Series G 300™ and Series G 750™ Potentiostat / Galvanostat / ZRA were used for the electrochemical measurements. Electrochemical Impedance Spectroscopy (EIS) studies were carried out using a three-electrode assembly with a saturated calomel reference electrode (SCE), a platinum counter electrode and the sample as working electrode in the form of a coupon with an exposed area of 10 mm × 5 mm. Only one 10 mm × 5 mm surface area was exposed to the test solution, the other surfaces being covered with Teflon tape, and allowed to establish a steady-state open circuit potential (OCP). EIS tests were performed in 0.1M NaCl solution at room temperature over a frequency range of 100 kHz to 0.2 Hz, using a 5 mV amplitude sinusoidal voltage. The 10 mm × 5 mm sample surface was immersed in the 0.1M NaCl solution (corrosion medium). All the measurements were performed at the open circuit potential (OCP). The impedance spectra were collected, and the experimental results were fitted to an equivalent circuit (EC) using the Echem Analyst™ data analysis software. The solution resistance (R_s), polarization resistance or charge transfer resistance (R_{ct}), and double layer capacitance (C_p) of the thermally treated alloys were determined.

As in the EIS tests, a three electrode cell arrangement was also used for the potentiodynamic polarization measurements. The selected potential range was from -1 to +1 V and the measurements were made at a scan rate of 0.50 mV/s. First the voltage was applied for 100 s to achieve steady state OCP, and the immersion time to invert the potential from -1 V to +1 V was about 67 min. The corrosion current density (i_{corr}, evaluated by the Butler-Volmer equation), corrosion potential (E_{corr}), pitting corrosion potential (E_{pit}) and corrosion rate (in mpy) were calculated from the Tafel curve. The tests were carried out at room temperature in solutions containing 0.1M of NaCl at a fixed and neutral pH value. No stirring was applied and the experiments were carried out in a closed cell. Corroded samples were cleaned in distilled water and examined with a scanning electron microscope (SEM) JEOL JSM-7600F.

Results and discussion

Impedance measurements

OCP ***versus*** **time behavior –** Large fluctuations in the open circuit potential were seen for the peakaged alloys in 0.1M NaCl solution (Table 1) during the first 100 s of exposure. Then the fluctuations decreased and the OCP reached an approximately steady state. The steady-state OCP of the Cu-free alloy was -0.8454 V and the occurrence of a positive shift in the OCP of the Al-6Si-0.5Mg alloy containing 4 wt.% Cu indicated the existence of anodically controlled reactions. The OCP values mainly depend on the chemical composition of the alloys.

The obtained data were modeled and the equivalent circuit that best fitted the results is shown in Fig. 1. R_s represents the ohmic resistance of the electrolyte. R_{ct} and C_p are the charge transfer resistance and electrical double layer capacitance, respectively, which correspond to Faradaic processes at the alloy/media interface. Nyquist curves for the suggested equivalent circuit model for the alloys in 0.1M NaCl solution are shown in Fig. 2. In Nyquist diagrams, the imaginary component of the impedance (Z'') against the real part (Z') is obtained in the form of a semi-circle for each sample.

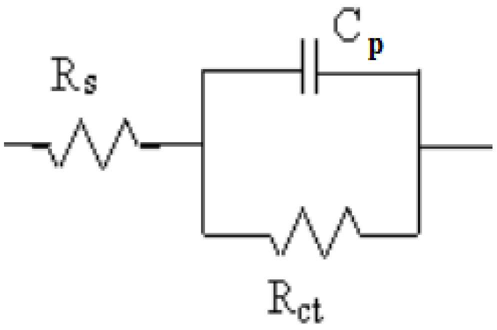

Fig. 1 Electrical equivalent circuit used for fitting of the impedance data of the alloys in 0.1M NaCl solution.

Table 1 Results of the EIS examination: solution resistance (R_s), charge-transfer resistance (R_{ct}), electrical double layer capacitance (C_p), open circuit potential (OCP).

Alloy	R_s (Ω)	R_{ct} (kΩ)	C_p (μF)	OCP (V/s)
Al-6Si-0.5Mg	40.37	15.57	1.259	-0.8454
Al-6Si-0.5Mg-4Cu	47.97	6.435	2.942	-0.6263

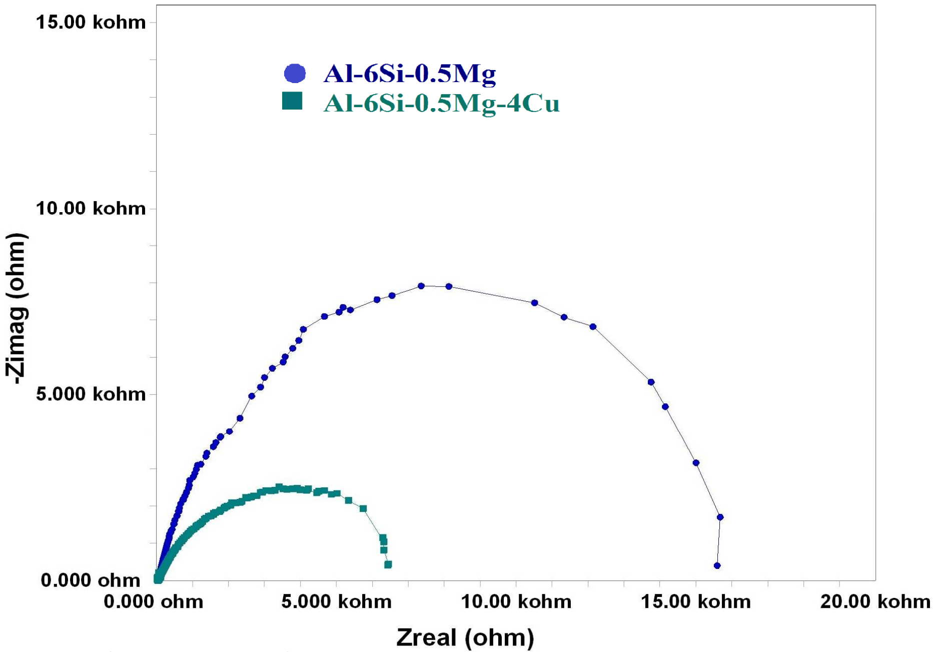

Fig. 2 Nyquist plot of the impedance for the aged alloys in 0.1M NaCl solution.

Table 1 shows the results obtained by Electrochemical Impedance Spectroscopy (EIS). The solution resistance of the alloys (R_s) changed from 40 to 48 Ω, *i.e.* the values are very similar. The impedance measurements showed that in 0.1M NaCl solution, 4 wt.% Cu in the Al-6Si-0.5Mg alloy decreased the charge transfer resistance. For the Cu-free Al-6Si-0.5Mg alloy, the charge transfer resistance (R_{ct}) in 0.1M NaCl solution was 15.57 kΩ, and this value was decreased to 6.435 kΩ by addition of 4 wt.% Cu. This decrease of the charge transfer resistance shows the decrease of the corrosion resistance of the alloy with Cu addition. Addition of 4 wt.% Cu caused a dramatic drop of the corrosion resistance of the Al-6Si-0.5Mg alloy because of overalloying and excessive intermetallic particles. The double layer capacitance (C_p) of the Cu-free Al-6Si-0.5Mg alloy was 1.259 µF; it increased to 2.942 µF with the addition of 4 wt.% Cu.

Fig. 3 shows the experimental EIS results for the alloys in a Bode magnitude diagram. Bode plots show the total impedance behavior against the applied frequency. At high frequencies, only the very mobile ions in solution are excited so that the solution resistance (R_s) can be assessed. At intermediate frequencies, capacitive charging of the solid-liquid interface occurs. The capacitive value C_p can provide very important information about oxide properties when passivation takes place or thicker oxides are formed on the surface. At low frequencies, the capacitive charging disappears because charge transfer or electrochemical reactions can occur and the measured value of the resistance corresponds directly to the corrosion rate. For this reason, the low frequency impedance value is referred to as polarization, or charge transfer resistance (R_{ct}).

Potentiodynamic polarization measurements

The potentiodynamic polarization curves of the alloys in 0.1M NaCl solution are shown in Fig. 4. In the anodic branch (>-583 mV), the anodic current density of the Al-6Si-0.5Mg alloy decreased with Cu addition. This decrement is caused by the slowing down of the anodic reaction of the Al-6Si-0.5Mg alloy due to the addition of Cu and formation of micro galvanic cells in the α-aluminum matrix. Different intermetallic compounds like Mg_2Si, Al_2Cu, *etc.*, can cause micro galvanic cells because of the difference in the corrosion potential between the intermetallics and the α-aluminum matrix [2,23,24]. The electrochemical parameters (i_{corr}, E_{corr}, E_{pit}, corrosion rate) obtained from the potentiodynamic polarization curves are presented in Table 2. The corrosion potential (E_{corr}) of the Al-6Si-0.5Mg alloy increased after addition of Cu.

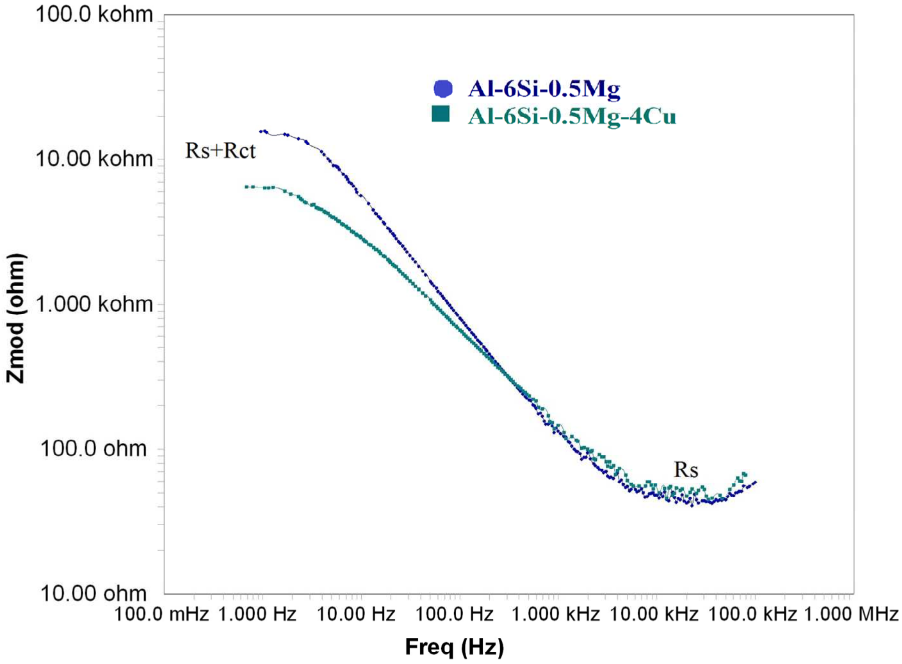

Fig. 3 Bode plot for the aged alloys in 0.1M NaCl solution.

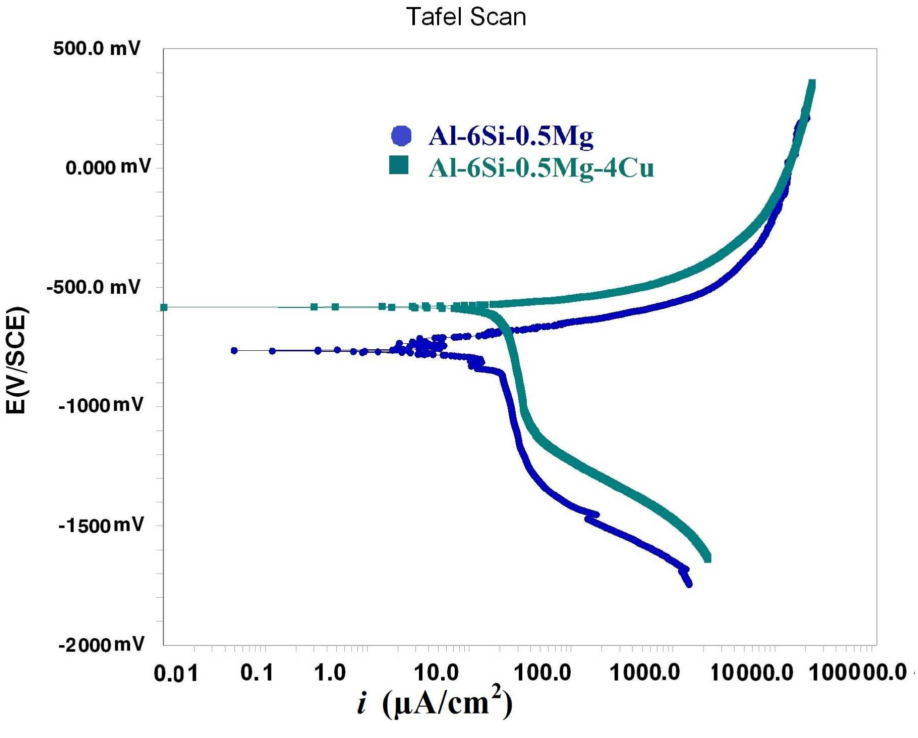

Fig. 4 Potentiodynamic polarization curves of the aged alloys in 0.1M NaCl solution.

Table 2 Results of the potentiodynamic polarization tests: corrosion current density (i_{corr}), corrosion potential (E_{corr}), pitting corrosion potential (E_{pit}), and corrosion rate.

Alloy	i_{corr} (μA/cm^2)	E_{corr} (mV)	E_{pit} (mV)	Corrosion rate (mpy)
Al-6Si-0.5Mg	6.300	-764	-480	5.287
Al-6Si-0.5Mg-4Cu	16.30	-583	-340	13.650

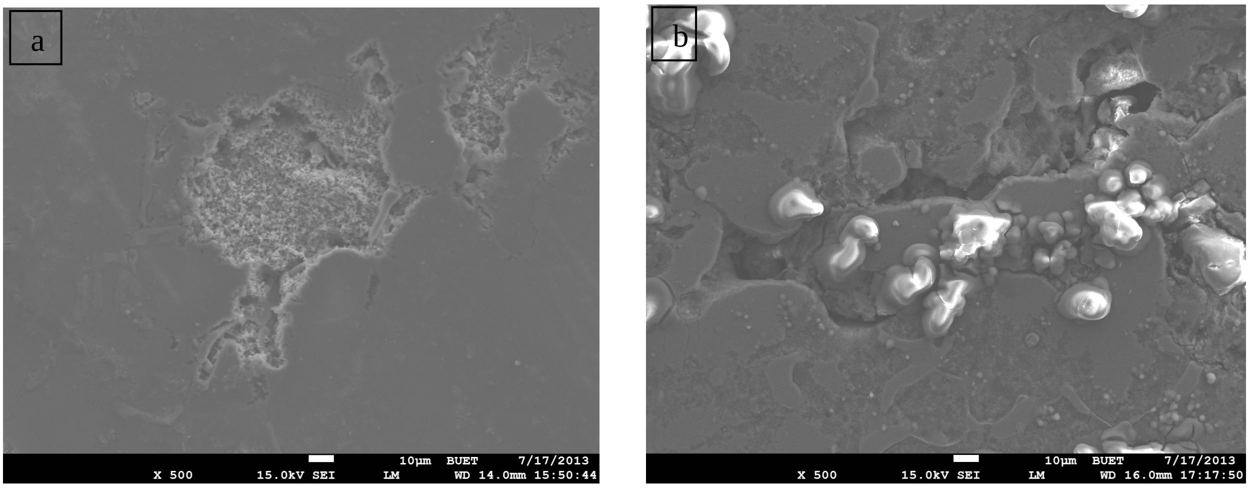

Fig. 5 SEM Secondary Electron Images of the damaged surface morphology of the (a) Al-6Si-0.5Mg and the (b) Al-6Si-0.5Mg-4Cu alloy in 0.1M NaCl solution (immersion time ~67 min at room temperature).

Indeed, in the Cu-free Al-6Si-0.5Mg alloy, the corrosion potential was -764 mV and with addition of 4 wt.% Cu the corrosion potential of the alloy was shifted towards a less negative value (-583 mV). The pitting potential of the Cu-containing alloy was also shifted towards less negative values. The current density (i_{corr}) of the Cu-free Al-6Si-0.5Mg alloy was 6.3 µA/cm^2 and the corrosion rate 5.287 mpy. The corresponding values for the alloy containing 4 wt.% Cu were 16.30 µA/cm^2 and 13.65 mpy, *i.e.* both these parameters increased when Cu was added.

Microstructural investigations

The microstructure of selected as-corroded samples, visualized by SEM, exhibited pronounced pits; showing that the samples had suffered pitting corrosion attacks. The exposed surface showed evidence of localized attacks at the locations of the intermetallics, caused by dissolution of the matrix. There was evidence of corrosion products in all the examined samples. It is probable that the pits are formed by intermetallics dropping out from the surface, due to dissolution of the surrounding matrix. However, it is also possible that the pits are caused by selective dissolution of intermetallics or particles of secondary phase precipitates. The samples were characterized by SEM after the potentiodynamic polarization tests. The peakaged Cu-free alloy exhibited pits on the surface, which apparently had nucleated randomly. The Cu-containing peakaged alloy was more susceptible to pitting corrosion than the Al-6Si-0.5Mg alloy. Figs. 5a and 5b clearly reveal that the pit density of the Al-6Si-0.5Mg-4Cu alloy is much higher than that of the Cu-free alloy. In Fig. 5.b, there seems to be uniform formation of surface pits, which are deeper than those in the Al-6Si-0.5Mg alloy.

Conclusions

The major type of corrosion exhibited by the automobile alloys immersed in NaCl solutions in the present work was pitting corrosion. It was found that the addition of 4 wt.% Cu to Al-6Si-0.5Mg alloys tends to diminish the excellent corrosion resistance of the Al-6Si-0.5Mg alloy in NaCl media. The open circuit potential (OCP), corrosion potential (E_{corr}), and pitting corrosion potential (E_{pit}) in NaCl solution were shifted in the more noble direction by the addition of Cu.

Conflicts of interest

The authors declare that there are no conflicts of interest. The authors are also thankful to PP & PDC, BCSIR, Dhaka, Bangladesh, for having carried out the electrochemical test.

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