Effect of Cu content on the Electrochemical Corrosion Behavior of Peak-aged Al-6Si-0.5Mg Alloys in Sodium Chloride Solution

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Abstract

The purpose of this study is to understand the electrochemical corrosion behavior of 1wt% Cu content Al-6Si-0.5Mg alloy in 0.1M NaCl solution. The potentiodynamic polarization curves reveal that 1wt% Cu content alloy is less prone to corrosion than the Cu free alloy. The EIS test results show that corrosion resistance or polarization resistance (R_{ct}) increases with the addition of 1wt% Cu to Al-6Si-0.5Mg alloy. Higher polarization resistance (R_p) has been obtained with the addition of 1wt% Cu to the Al-6Si-0.5Mg alloy. Due to addition of Cu and thermal modification, the magnitude of open circuit potential (OCP), corrosion potential (E_{corr}) and pitting corrosion potential (E_{pit}) of Al-6Si-0.5Mg alloy in NaCl solution were shifted to the more noble direction.

Keywords: Al-6Si-0.5Mg Alloy; Cu addition; Electrochemical Corrosion.

INTRODUCTION

Aluminium and its alloys are considered to be highly corrosion resistant under the majority of service conditions [1].The various grades of pure aluminium are the most resistant, followed closely by the Al-Mg and Al-Mn alloys. Next in order are Al-Mg-Si and Al-Si alloys. The alloys containing copper are the least resistant to corrosion[2], but this can be improved by coating each side of the copper containing alloy with a thin layer of high purity aluminium, thus gaining a three ply metal (Alclad). This cladding acts as a mechanical shield and offers sacrificial protection[3].When aluminum surfaces are exposed to atmosphere, a thin invisible oxide (Al_2O_3) skin forms, which protects the metal from further corrosion in many environments[1]. This film protects the metal from further oxidation unless this coating is destroyed, and the material remains fully protected against corrosion[3]. The composition of an alloy and its thermal treatment are important do determine the susceptibility of the alloy to corrosion[4,5].

Over the years a number of studies have been carried out to assess the effect of Cu content and the distribution of second phase intermetallic particles on the corrosion behavior of Al alloys. The distribution of Cu in the microstructure affects the susceptibility to localized corrosion. Intergranular corrosion (IGC) is generally believed to be associated with Cu containing grain boundary precipitates and the precipitates free zones (PFZ) along grain boundaries[6-8]. In heat treatable Al-Si-Mg(-Cu) series alloys the susceptibility to localized corrosion [pitting and / or intergranular (IGC)] and the extent of attack are mainly controlled by the type, amount and distribution of the precipitates which form in the alloy during any thermal or thermomechanical treatment performed during manufacturing processes[6-10].

Depending on the composition of the alloy and parameters of the heat treatment process, these precipitates form in the bulk of the grain, or in the bulk as well as 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 Si content in the alloy exceeds the Mg_2Si stoichiometry [2,11-12].

It has demonstrated that in Al-Cu-Si alloys a more finely and homogeneously distributed Al_2Cu and needle-like Si particles in the ternary eutectic mixture, tend to improve the corrosion resistance mainly due to the galvanic protection of both Al_2Cu and Si phases [13]. Although it has also been reported[13, 14] that fine Si particles tends to decrease the corrosion resistance of binary Al-Si alloys when associated with the Al2Cu intermetallic phase, a better galvanic protection is provided for finer Al-Cu-Si alloy microstructures. It was also reported that the ternary eutectic mixture consisting of Al + Al_2Cu + Si phases is nobler than the Al-matrix and Al-phase in the eutectic mixture[15].

The present study is an attempt to understand the electrochemical corrosion behavior of 1wt%Cu content Al-6Si-0.5Mg alloys in 0.1M NaCl solution. The corroded surfaces of the alloys were examined after exposure using a scanning electron microscopy (SEM) to understand better the corrosion mechanisms.

EXPERIMENTAL
A. Materials Preparation
The Al-6Si-0.5Mg(-0.5Cu) alloys were prepared by melting Al-7Si-0.3Mg (A356) alloys and adding Al, Cu and Mg into the melt. The melting operation was carried out in a gas fired clay graphite crucible furnace and the alloys were cast in a permanent steel mould. After solidification the alloys were homogenized (500^0C for 24hr), solution treated (540^0C for 2hr) and finally artificially aged (225^0C for 1hr). After heat treatment rectangular samples (30mm x 10mm x 5mm) were prepared for metallographic observation and subsequent electrochemical test. Deionized water and analytical reagent grade sodium chloride (NaCl) were used for the preparation of 0.1M solution. All measurements were carried out at room temperature.

B. Potentiodynamic Polarization Measurements
A computer-controlled Gamry Framework TM Series G 300™ and Series G 750™ Potentiostat/ Galvanostat/ZRA was used for the electrochemical measurements. The Potentiodynamic polarization studies were configured in cells, using three-electrode assembly: a saturated calomel reference electrode, a platinum counter electrode and the sample in the form of coupons of exposed surface area of $0.50cm^2$ (10mm x 5mm) as working electrode. Only one 10mm x 5mm surface was exposed to the test solution, the other surfaces being covered with Teflon tape. The system was allowed to establish a steady-state open circuit potential (OCP). The potential range selected was -1 to +1V and measurements were made at a scan rate of 0.50mV/s. The corrosion current (I_{corr}), corrosion potential (E_{corr}), pitting corrosion potential (E_{pit}) and corrosion rate (mpy) were calculated from Tafel curve. The tests were carried out at room temperature in solutions containing 0.1M of NaCl at a fixed and neutral pH value. The corroded samples were cleaned in distilled water and examined under scanning electron microscope(SEM).

C. *Electrochemical Impedance Measurements*

As in potentiodynamic polarization test, three electrode cell arrangements were also used in electrochemical impedance measurements. Rectangular samples (10mm x 5mm) were connected with copper wire and adopted as working electrode. EIS tests were performed in 0.1M NaCl solution at room temperature over a frequency range of 100kHz to 0.2Hz using a 5mV amplitude sinusoidal voltage. The 10mm x 5mm sample surface was immersed in NaCl solution (corrosion medium). All the measurements were performed at the open circuit potential (OCP). The test cells were maintained at room temperature and the NaCl solution was refreshed regularly during the whole test period. The impedance spectra were collected, fitting the experimental results to an equivalent circuit (EC) using the Echem AnalystTM data analysis software and evaluating the solution resistance (R_s), polarization resistance (R_{ct}) and double layer capacitance(C_p) of the thermal treated alloys.

RESULTS AND DISCUSSION

A. *Impedance Measurements*

TABLE I.   Electrochemical Impedance Spectroscopy (EIS) test results.

Alloy Compositions	R_s [Ω]	R_p [$k\Omega$]	C_p [μF]	OCP [V/SCE]
Al-6Si-0.5Mg	40.37	15.57	1.259	-0.8454
Al-6Si-0.5Mg-1Cu	44.08	27.13	3.219	-0.6534

The open circuit potential (OCP) with exposure time of aged Al-6Si-0.5Mg/Al-6Si-0.5Mg-1Cu alloys in 0.1M NaCl solution is shown in Table I. The steady state OCP of Cu free alloy Al-6Si-0.5Mg is -0.8454 V and it is more negative between the alloys under investigation. The positive shift in OCP in the Al-6Si-0.5Mg-1Cu alloy indicates the existence of anodically controlled reaction. The OCP values mainly depend on the chemical compositions and thermal history of the alloys.

The data obtained were simulated and the equivalent circuit that best fitted to the experimental data is shown in Figure 1. R_s, R_{ct} and C_p represent the ohmic solution resistance of the electrolyte, polarization resistance and electrical double layer capacitance respectively. Figure 2 shows the Nyquist diagrams (suggested equivalent circuit model shown in Figure 1) of the Al-6Si-0.5Mg/Al-6Si-0.5Mg-1Cu alloys in 0.1M NaCl in de-mineralized (DM) water. In Nyquist diagrams, the imaginary component of the impedance (Z") against real part (Z') is obtained in the form of capacitive-resistive semicircle for each sample.
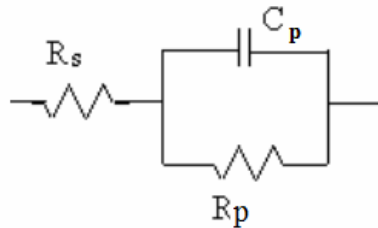

Fig. 1. Electrical equivalent circuit used for fitting of the impedance data of alloys in 0.1M NaCl solution.
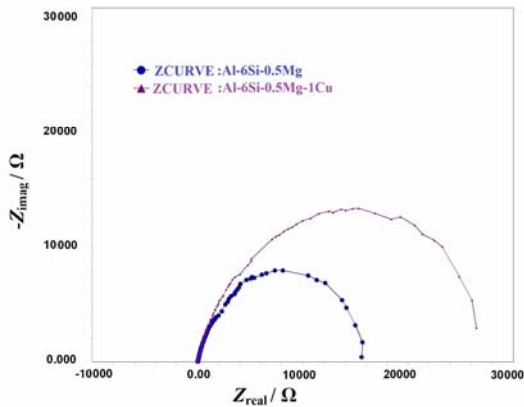
Fig. 2. Nyquist plots for the artificially aged Al-6Si-0.5Mg (-1Cu) alloys in 0.1M NaCl solution.
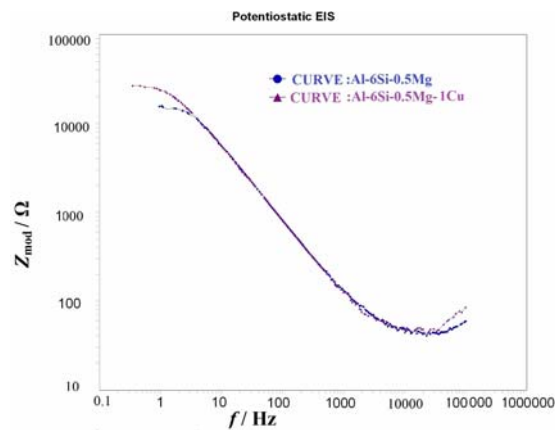

Fig. 3. Bode plots for the artificially aged Al-6Si-0.5Mg (-1Cu) alloys in 0.1M NaCl solution.

Figure 3 shows the experimental EIS results in Bode magnitude diagram for Al-6Si-0.5Mg/Al-6Si-0.5Mg-1Cu alloys. Bode plots show the total impedance behavior against 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 lower intermediate frequencies, capacitive charging of the solid-liquid interface occurs. The capacitive value C_p can provide very important information about oxide properties when passivated or thicker oxides are formed on the surface. At low frequency, the capacitive charging disappears because the charge transfer of electrochemical reaction can occur and this measured value of the resistance corresponds directly to the corrosion rate. For this reason, this low frequency impedance value is referred to as polarization resistance (R_p).

The solution resistance of the alloys varies from 40-44Ω and there are insignificant changes of R_s values for the alloys during EIS testing. The R_s values are negligible with respect to R_p and the electrolyte behaves as a good ionic conductor. Impedance

measurements showed that in 0.1M NaCl solution, addition of 1 wt% Cu in the Al-6Si-0.5Mg alloy increased the polarization resistance (R_p). For the Cu free Al-6Si-0.5Mg alloy, the polarization resistance (R_p) value in 0.1M NaCl solution is 15.57kΩ, and this is increased to 27.13kΩ with the addition of 1wt% Cu to the Al-6Si-0.5Mg alloy. The increase in the polarization resistance indicates an increase in the corrosion resistance of the alloys with Cu addition. The double layer capacitance (C_p) of the Cu free Al-6Si-0.5Mg alloy is 1.259μF. The double layer capacitance of Al-6Si-0.5Mg alloy increased with an addition of 1 wt% Cu.

B. *Potentiodynamic Polarization Measurements*

Table II. shows the potentiodynamic polarization test results obtained from the electrochemical tests.

TABLE II.   Potentiodynamic polarization test results

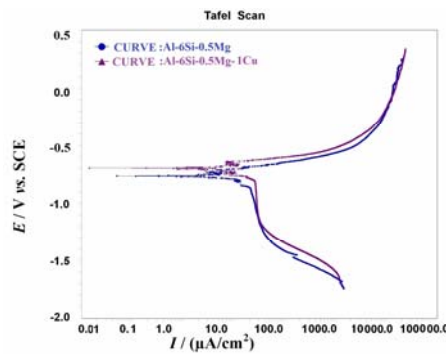| *Alloy Compositions*	*I_{corr}* [μA/cm²]	*E_{corr}* [mV]	*E_{pit}* [mV]	*Corrosion rate* [mpy]
Al-6Si-0.5Mg	6.300	-764	-480	5.287
Al-6Si-0.5Mg-1Cu	2.950	-697	-370	2.474

Fig. 4. Potentiodynamic polarization curves of the peak-aged alloys.

Potentiodynamic polarization curves of Al-6Si-0.5Mg/Al-6Si-0.5Mg-1Cu alloys in 0.1M NaCl solution are shown in Figure 4. Anodic current density of Al-6Si-0.5Mg alloy decreased with Cu addition. This is caused by the slowing of the anodic reaction of Al-6Si-0.5Mg-1Cu alloy. The addition of Cu caused the formation of micro-galvanic cells in α-aluminium matrix. The different intermetallic compounds (like Mg_2Si, Al_2Cu etc.) can lead to the formation of micro-galvanic cells because of the difference of corrosion potential between intermetallics and α-aluminium matrix. Park [16] has reported that the addition of Cu increased the corrosion potential of a number of Al–Cu–Si alloys. For the Cu free Al-6Si-0.5Mg alloy corrosion potential is -764mV, which is more negative potential between the alloys investigated. With the addition of Cu, the corrosion potential of the alloy shifted towards more positive value. Pitting potential (E_{pit}) of the Cu content alloy also shifted towards more positive value (from -480 mV to -370 mV). Potentiodynamic tests showed that in 0.1M NaCl solution, addition of Cu in the Al-6Si-0.5Mg alloy decreased the corrosion current (I_{corr}). For the Cu free Al-6Si-0.5Mg alloy, the corrosion current (I_{corr} value) in 0.1M NaCl solution was 6.3 μA/cm², and this decreased to 2.950 μA/cm² with the addition of 1 wt% Cu and the corresponding corrosion rate of the Al-6Si-0.5Mg-1Cu alloy decreased to 2.474mpy.

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C. *Microstructural Investigation*

The microstructure of some selected as-corroded samples was observed under SEM. There was evidence of corrosion products of intermetallic compounds in all the samples examined. Besides, several pits were visible in all the samples examined. It is probable that the pits are formed by the intermetallics dropping out from the surface due to the dissolution of the surrounding matrix. However, it is also possible that the pits are caused by selective dissolution of the intermetallic/or particles of the second phase precipitates. Consequently, the forms of corrosion of the Al-6Si-0.5Mg/Al-6Si-0.5Mg-1Cu alloys were slightly uniform and predominantly pitting corrosion were characterized by SEM following potentiodynamic polarization tests. The peak-aged Cu free alloy (Al-6Si-0.5Mg) exhibited pits on their surface (Figure 5a), which apparently had nucleated randomly. Conversely, the exposed surface of the alloys exhibited a corrosion product covering the surface after polarization. There are more and severe pits in Cu free Al-6Si-0.5Mg alloy compared to that of Al-6Si-0.5Mg-1Cu alloy.
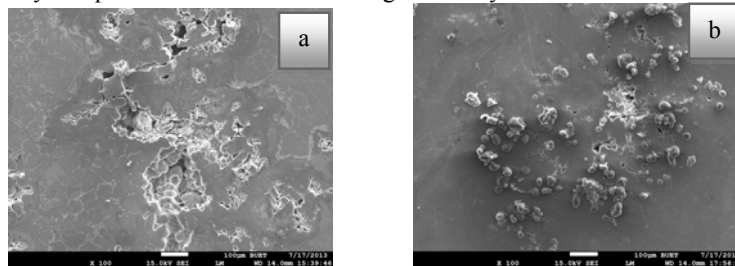

Fig. 5. SEM images show the damage surface morphology of as-corroded T6 aged (a) Al-6Si-0.5Mg and (b) Al-6Si-0.5Mg-1Cu alloys.

CONCLUSIONS

The EIS tests have shown that the addition of 1wt%Cu to Al-6Si-0.5Mg alloy has increased the corrosion resistance of Al-6Si-0.5Mg alloy by about two times in NaCl media. The linear polarization and Tafel extrapolation plot show that the corrosion current (I_{corr}) and corrosion rate (mpy) decrease with the addition of 1 wt% Cu to Al-6Si-0.5Mg alloy. The open circuit potential (OCP), corrosion potential (E_{corr}) and pitting corrosion potential (E_{pit}) in the NaCl solution were shifted in the more noble direction due to Cu addition. The forms of corrosion in the studied Al-6Si-0.5Mg/Al-6Si-0.5Mg-1Cu alloys are pitting corrosion in nature as obtained from the microstructural study. SEM observations show that the corrosion effect on the Cu free Al-6Si-0.5Mg alloy is more drastic when compared to corresponding Al-6Si-0.5Mg-1Cu alloy.

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