

The Effects of 2wt% Cu Addition on the Corrosion Behavior of Heat Treated Al-6Si-0.5Mg-2Ni Alloy

A. Hossain, M. A. Gafur, F. Gulshan, A. S. W. Kurny

Abstract—Al-Si-Mg-Ni(-Cu) alloys are widely used in the automotive industry. They have the advantage of low weight associated with low coefficient of thermal expansion and excellent mechanical properties – mainly at high temperatures. The corrosion resistance of these alloys in coastal area, particularly sea water, however is not yet known. In this investigation, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization have been used to evaluate the corrosion resistance of Al-6Si-0.5Mg-2Ni (-2Cu) alloys in simulated sea water environments. The potentiodynamic polarization curves reveal that 2 wt% Cu content alloy (Alloy-2) is more prone to corrosion than the Cu free alloy (Alloy-1). But the EIS test results showed that corrosion resistance or charge transfer resistance (R_{ct}) increases with the addition of Cu. Due to addition of Cu and thermal treatment, the magnitude of open circuit potential (OCP), corrosion potential (E_{corr}) and pitting corrosion potential (Epit) of Al-6Si-0.5Mg-2Ni alloy in NaCl solution were shifted to the more noble direction.

Keywords—Al-Si alloy, potentiodynamic polarization, EIS, SEM.

I. INTRODUCTION

THE increasing demand from many industries for improved properties in materials has stimulated the development of new materials. For the automotive industry, the properties most required are reduced weight, low thermal expansion coefficient and excellent mechanical properties; mainly wear resistance at high temperatures. In this context, various new materials such as the Al-Si alloys have been considered. Despite the excellent mechanical and physical properties of the Al-Si-Mg alloys, their corrosion resistance in aggressive environments is not yet well known. In recent years some work has been carried out to evaluate the corrosion resistance of these alloys in different media [1], [2].

Aluminium and its alloys are considered to be highly corrosion resistant under the majority of available service condition. The Al alloy containing copper are the least resistant to corrosion; 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, i.e. Alclad. This cladding acts as a mechanical shield and also protects the material by sacrificial. When aluminium surface is

expose to atmosphere, a thin invisible oxide (Al_2O_3) skin forms, which protects the metal from the corrosion in many environments. This film protect the metal from further oxidation unless this coating is destroyed, the material remains fully protected against corrosion. The composition of an alloy and its thermal treatment are of important for susceptibility of alloys to corrosion [3].

Over the years a number of studies have been carried out in order to assess the effect of Cu content and the distribution of second phase intermetallic particles on the corrosion behavior of Al alloys. The Cu distribution in the microstructure affects the susceptibility to localized corrosion. Pitting corrosion is usually occurs in the Al matrix near Cu containing intermetallic particles owing to galvanic interaction with Al matrix. Intergranular corrosion (IGC) is generally believed to be associated with Cu containing grain boundary precipitates and the PFZ along grain boundaries [2]-[4]. In heat treatable Al-Si-Mg(-Cu) series alloys, it was found that, 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 treatments performed during manufacturing processes [5]-[9]. In Ni-containing alloys the eutectic phase E consists of more or less soft 'eutectic Al (αE)' and hard 'eutectic Si and Al_3Ni ' [10]. When Ni is added to the Al-Si system, the eutectic transformation is characterized by a simultaneous formation of eutectic Si and Al_3Ni and consequently, eutectic Si and Al_3Ni form a geometrically entangled system. During the course of a solution treatment eutectic Al_3Ni does not significantly change its shape, as can be metallographically observed. Furthermore, in the presence of Ni-aluminides the loss of interconnectivity of eutectic Si is significantly reduced [11], [12].

In Al-Si-Mg alloys with increasing Ni concentration up to 2%, whereas the positive effect of Ni is much more considerable for the solution-treated alloys, especially with respect to the yield strength. While for Ni-containing alloys the contiguity of the 'eutectic Si and Al_3Ni ' is more or less preserved due to the presence of Ni-aluminides, the spheroidization of the eutectic Si in the Ni-free alloy ($AlSi_2(Mg)$) results in its reduced contiguity and thus reduced strength [11], [12]. 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 (Al_2Cu) Q-phase ($Al_4Mg_8Si_7Cu_2$), β -

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phase (Mg_2Si) and free Si if Si content in the alloy exceeds the Mg_2Si stoichiometry [13], [14].

Electrochemical measurements were recorded to characterize the electrochemical behavior of the Al-6Si-0.5Mg-2Ni (-2Cu) alloys. The corroded surfaces of alloys were examined after exposure using a scanning electron microscope (SEM) to understand better the corrosion mechanisms.

II. EXPERIMENTAL PROCEDURE

A. Materials Preparation

The alloys were prepared and the chemical compositions of the alloys are given in Table I. The experimental cast samples were first ground properly to remove the oxide layer from the surface. The sample were homogenised ($500^\circ C$ for 24 hr) and solutionized ($540^\circ C$ for 2hr) and finally peakaged ($225^\circ C$ for 1 hr). After heat treatment the rectangular samples (30mm x 10mm x 5mm) were prepared for metallographical observation and finally subjected to electrochemical test. Deionized water and analytical reagent grade sodium chloride (NaCl) were used for 0.1M solution preparation.

B. Potentiodynamic Polarization Measurements

A computer-controlled Gamry Framework TM Series G 300™ and Series G 750™ Potentiostat/ Galvanostat/ZRA were used for the electrochemical measurements. The Potentiodynamic polarization studies were configured in cells (Fig. 1), using three-electrode assembly with a saturated calomel reference electrode, a platinum counter electrode and the sample as working electrode in the form of coupons of exposed area of 0.50 cm^2 or 10mm x 5mm.

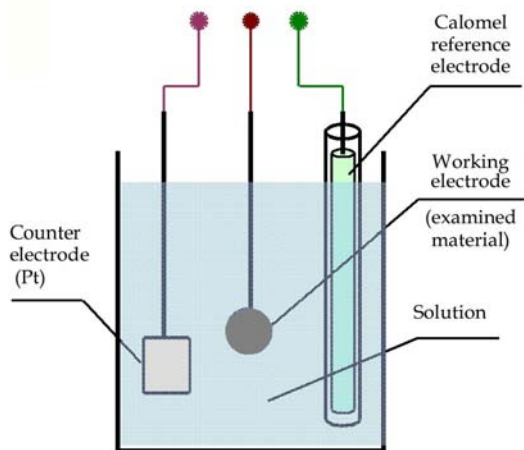


Fig. 1 Schematic representation of the three electrode system cell

Only one 10mm x 5mm surface area was exposed to the test solution and the other surfaces were covered with Teflon tape and 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 0.50 mV/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 by 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 electrodes for impedance measurements. 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 5mV amplitude sinusoidal voltage. The 10mm x 5mm sample surface was immersed in 0.1M 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 Analyst™ data analysis software and evaluating the solution resistance (R_s), polarization resistance or charge transfer resistance (R_{ct}) and double layer capacitance (C_p) of the thermal treated alloys.

The chemical compositions of the two alloys are shown in Table I.

TABLE I
CHEMICAL COMPOSITIONS OF THE EXPERIMENTAL ALLOYS

Alloy	Si	Mg	Ni	Cu	Ti	Sb	Al
Alloy-1	5.965	0.454	2.202	0.007	0.088	0.008	Bal
Alloy-2	5.760	0.501	2.001	1.968	0.081	0.005	Bal

Remarks: Alloy-1: Al-6Si-0.5Mg-2Ni; Alloy-2: Al-6Si-0.5Mg-2Ni-2Cu

III. RESULTS AND DISCUSSION

A. Impedance Measurements

Table II shows the Electrochemical Impedance Spectroscopy (EIS) results obtained from the electrochemical tests.

TABLE II
IMPEDANCE TEST RESULTS

Alloy Code	$R_s(\Omega)$	$R_{ct}(k\Omega)$	$C_p(\mu F)$	OCP(V/SCE)
Alloy-1	40.53	14.44	1.645	-0.6814
Alloy-2	44.40	27.95	1.773	-0.6445

The open circuit potential (OCP) with exposure time of aged Al-6Si-0.5Mg-2Ni (-2Cu) alloys in 0.1M NaCl solution is shown in Table II. Large fluctuations in open circuit potential for the alloys were seen during the time of 100s exposure. Afterwards the OCP fluctuation decreased and reached about steady state after a period of exposure. The steady state OCP of Cu free alloy (Alloy-1) is -0.6814 V and it is the negative OCP value of other alloys. The occurrence of a positive shift in the OCP of 2wt% Cu added to Al-6Si-0.5Mg-2Ni alloy indicates the existence anodically controlled

reaction. The OCP values mainly depend on the chemical compositions and thermal history of the alloys.

The data obtained were modeled and the equivalent circuit that best fitted to the experimental data is shown in Fig. 2. R_s represent the ohmic solution resistance of the electrolyte. R_{ct} and C_p are the charge transfer resistance and electrical double layer capacitance respectively, which correspond to the Faradaic process at the alloy/media interface. Fig. 3 shows the Nyquist diagrams of the Alloys 1 and 2 in 0.1M NaCl in demineralized (DM) water. Nyquist curves with suggested equivalent circuit model for the alloys in 0.1M NaCl solution is shown in Fig. 2. 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.

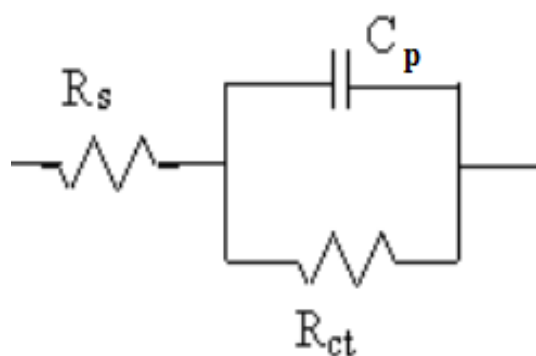


Fig. 2 Electrical equivalent circuit used for fitting of the impedance data of Alloys 1 and 2 in 0.1M NaCl solution

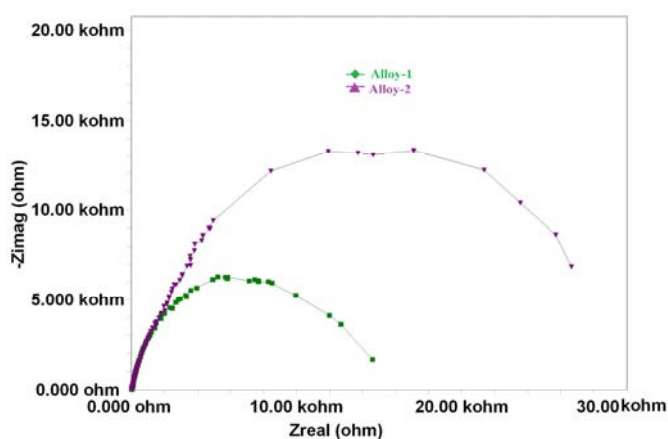


Fig. 3 Nyquist plot for the aged Alloys 1 and 2 in 0.1M NaCl solution

The solution resistance of the alloys varies from 40-44 Ω and the R_s values of the alloys are very similar to each other. So there are insignificant changes of R_s values for the alloys during EIS testing. The solution resistance is negligible with respect to R_{ct} and the electrolyte behaves as a good ionic conductor. Impedance measurements showed that in 0.1M NaCl solution, addition of 2wt%Cu in the Al-6Si-0.5Mg alloy increases the charge transfer resistance (R_{ct}). For the Cu free Al-6Si-0.5Mg-2Ni alloy (Alloy-1), the charge transfer resistance (R_{ct}) value in 0.1M NaCl solution is 14.44k Ω , and

this is increased to 27.95k Ω with the addition of 2wt% Cu to the Al-6Si-0.5Mg-2Ni alloy. The increase in the charge transfer resistance indicates an increase in the corrosion resistance of the Al-6Si-0.5Mg-2Ni alloy with Cu addition. The double layer capacitance (C_p) of the Cu free Al-6Si-0.5Mg-2Ni alloy (Alloy-1) is 1.645 μ F, which is the lower value between the alloys investigated.

B. Potentiodynamic Polarization Measurements

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

TABLE III
 POTENTIODYNAMIC POLARIZATION TEST RESULTS

Alloy Code	I_{corr} (μ A)	E_{corr} (mV)	E_{pit} (mV)	Corrosion rate(mpy)
Alloy-1	2.540	-720	-426	2.132
Alloy-2	2.710	-644	-360	2.278

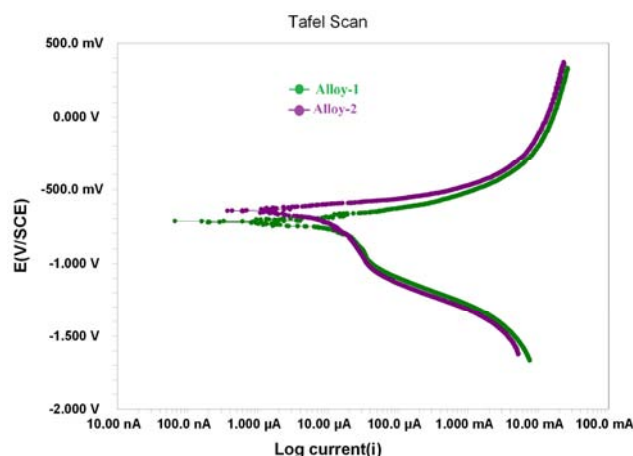


Fig. 4 Potentiodynamic polarization curves of aged Alloys 1 and 2 in 0.1M NaCl solution

Potentiodynamic polarization curves of the Alloys 1 and 2 in 0.1M NaCl solution are shown in Fig. 4. Anodic current density of Al-6Si-0.5Mg-2Ni alloy decreased with Cu addition. This decrement is caused by slowing of the anodic reaction of Al-6Si-0.5Mg-2Ni-2Cu alloy due to the addition of Cu and micro galvanic cells caused in α -aluminum matrix with adding of Cu. Different intermetallic compounds like Mg_2Si , Al_2Cu , Al_3Ni etc. can cause micro galvanic cells because of the difference of corrosion potential between intermetallics and α -aluminum matrix. The corrosion potential (E_{corr}) value increased with the addition of 2wt%Cu in Al-6Si-0.5Mg-2Ni alloy. For the Cu free Al-6Si-0.5Mg-2Ni alloy (Alloy-1) corrosion potential is -720mV, which is the higher negative potential between the alloys investigated. With the addition of Cu, corrosion potential of the alloy (Alloy-2) shifted towards more positive values. Pitting potential (E_{pit}) of the Alloy-2 also shifted towards more positive values (from -426 mV to -360mV). Potentiodynamic tests showed that in 0.1M NaCl solution, Adding 2wt%Cu in the Al-6Si-0.5Mg-2Ni alloy increases the corrosion current (I_{corr}). For the Cu free Al-6Si-0.5Mg-2Ni alloy (Alloy-1), the corrosion current (I_{corr}) value in 0.1M NaCl solution is 2.540 μ A, and this

increased to 2.710 μ A with the addition of 2wt% Cu to the Al-6Si-0.5Mg-2Ni alloy. And the corresponding corrosion rate increases for the Alloy-2 (2.278mpy).

C. Microstructural Investigation

The microstructure of some selected as-corroded samples after electrochemical corrosion study using SEM indicates some pronounced pits; indicating that the samples have suffered pitting corrosion attack. The exposed surface shows evidence of localized attack at the location of the intermetallic caused by the dissolution of the matrix.

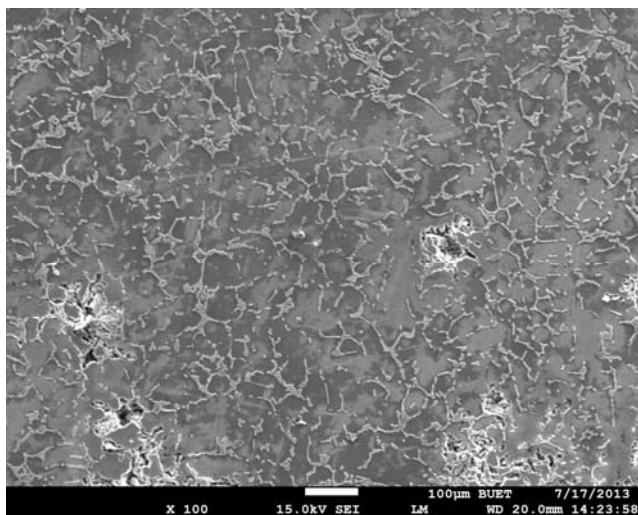


Fig. 5 SEM images show the damage surface morphology of as-corroded T6 aged Alloy-1 in 0.1M NaCl solution

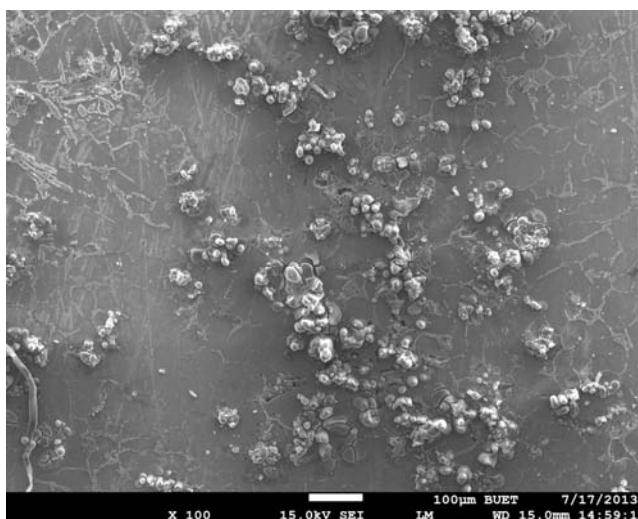


Fig. 6 SEM images of the damage surface morphology of as-corroded T6 peakaged Alloy-2 in 0.1M NaCl solution

There was evidence of corrosion products of intermetallic compounds in all the samples examined. Besides, several pits are visible in all samples examined. It is provable that the pits are formed by intermetallic 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 in the studied Al-6Si-0.5Mg-2Ni (-2Cu) alloys are slightly uniform and predominantly pitting corrosion as obtained by the SEM. Samples were characterized by SEM following potentiodynamic polarization tests. The peakaged Cu free alloy (Alloy-1) exhibited pits on their surface (Fig. 5), which apparently had nucleated randomly. Conversely, the exposed surface of the alloys exhibited a corrosion product with covering the surface after polarization. All the micrographs (Figs. 5 and 6) also showed that there was no corrosion in the fragmented and modified Al-Si eutectics.

IV. CONCLUSIONS

From the EIS test, the corrosion resistance, R_{ct} value as an impedance parameter of the alloys shows a higher at 2 wt% Cu into Al-6Si-0.5Mg-2Ni alloy. From the linear polarization and Tafel extrapolation plot, the I_{corr} and corrosion rate (mpy) increase with the addition of 2wt% Cu into Al-6Si-0.5Mg-2Ni 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 2wt%Cu additions into Al-6Si-0.5Mg-2Ni alloy. Consequently, the forms of corrosion in the studied alloys are pitting corrosion as obtained from the microstructures study with pits observations.

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