

ELECTROCHEMICAL CORROSION BEHAVIOR OF AL-SI HYPOEUTECTIC ALLOY IN SIMULATED SEAWATER ENVIRONMENT

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ABSTRACT

The aim of this study is to investigate the corrosion behavior of artificially peakaged Al-Si hypoeutectic alloy in simulated seawater environment. The electrochemical corrosion behavior of the thermal treated Al-Si alloy in simulated seawater was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. A representative set of samples was recovered and laboratory tests performed to evaluate the type and degree of corrosion attack. In potentiodynamic polarization test corrosion rate, current, potential and morphology were revealed. Corrosion resistance or charge transfer resistance (R_{ct}) and simulated seawater resistance assessed by electrochemical impedance spectroscopy (EIS) test. Optical Light Microscopy (OLM) and Scanning Electron Microscopy (SEM) were employed to characterize the corroded surface and to observe the extent of pitting. Pronounced effect of pitting was observed in presence of Cl⁻ for Al-Si alloy.

Keywords: Al-6Si alloy; electrochemical corrosion; scanning electron microscopy (SEM)

INTRODUCTION

Al-Si alloys with silicon as a major alloying element constitute a class of material, which provides the most significant part of all shaped castings manufactured, especially in the aerospace and automotive industries. Al-Si Alloy make composite have become a substitute material in automobile industries especially in making of piston, cylinder blocks and other engineering components. They are also being considered as a potential in making of impellers, agitators etc. in marine structural applications because of their enhanced physical, mechanical and tribological properties (Singh et al., 2010; Shabestari and Moemeni, 2004). Al-Si alloys with silicon as a major alloying element constitute a class of material, which provides the most significant part of all shaped castings manufactured, especially in the aerospace and automotive industries. This is mainly due to the outstanding effect of silicon in the improvement of casting characteristics, combined with other physical properties such as mechanical properties and corrosion resistance. In general, an optimum range of silicon content can be assigned to casting processes (Rooy, 1988; Shabestari and Moemeni, 2004). Owing to their light weight, suitable strength and strong resistance to corrosion, aluminum alloys are used in a broad spectrum of engineering applications. The corrosion resistance of aluminum is attributed to an exceptionally stable oxide film that forms on its surface. This film is resistant to attack from water and oxygen in a wide range of temperatures and pH levels, making aluminum alloys useful in a variety of environments (Claycomb and Sherwood, 2004).

However, service life of any material mainly depends on its corrosion resistance in the surrounding environment. For example, if Al-Si alloy make AMC are used in marine environment, their susceptibility to pitting corrosion is likely to be increased in the presence of chlorides ions. The presence of aggressive ions like chloride creates extensive localized attack Chloride ions adsorb on the metal surface and destroy the existing passive oxide film that leads to a localized attack in the form of pitting corrosion. Since pitting corrosion is a main problem of AMC, different approaches have been made to control pitting corrosion by halide ions (Garrigues et al., 1995; Singh et al., 2010). In addition, it is well known that the corrosion behavior of aluminum alloys is significantly affected

by the presence of particles in the matrix. Particles that contain Al, Cu and Mg tend to be anodic relative to the alloy matrix, while those that contain Al, Cu, Fe and Mn tend to be cathodic relative to the matrix (Wei et al., 1998). Although the metallurgical and micromechanical aspects of the factors controlling microstructure, unsoundness, strength and ductility, and corrosion resistance of alloys are complex, it is well known that solidification processing variables are of high order of importance. The cooling rate during solidification defines the fineness of the dendritic network. The solute redistribution, the anodic or cathodic electrochemical behaviour of each component of the alloy and the scale of dendrite spacings and thermal treatment are the main microstructural characteristics affecting the corrosion resistance of the alloy (Osório et al., 2011).

The increasing demand from many industries for improved properties in materials has stimulated the development of new materials. 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 (Staley and Lege, 1993; Anand et al., 1997; Traldi et al., 2001; Traldi et al.2003).

The aim of this research paper is to evaluate the electrochemical corrosion properties Al-6Si heat treated alloy in simulated seawater environment.

EXPERIMENTAL PROCEDURE

Materials preparation

The Al-6Si alloy was utilized by melting Al-7Si-0.3Mg (A356) alloy and adding Al into the melt. After casting and solidification into a permanent steel mould of the alloy, suitable specimens were cut and used for the experiments. The samples were homogenised (500°C for 24hr) and solutionized (540°C for 2hr) and finally artificially aged (225°C for 1hr). 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 preparation of 0.1M simulated seawater. All measurements were carried out at room temperature.

Electrochemical Measurements

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 cm² or 10mm x 5mm. 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. First 100s applied for achieving steady state OCP and for potential -1V to +1V immersion time was about 67 minutes. The corrosion current (I_{corr} , measured by Butler-Volmer equation), 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. No stirring applied and the experiments carried out in a closed cell. The corroded samples were cleaned in distilled water and examined by optical light and scanning electron microscope.

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 alloy.

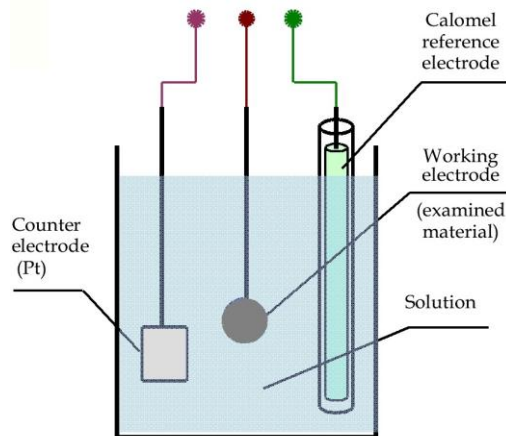


Fig. 1: Schematic representation of the three-electrode system cell

RESULTS AND DISCUSSION

Impedance Measurements

Table 1. shows the Electrochemical Impedance Spectroscopy (EIS) test results.

Table 1: Impedance test results

Alloy Code	$R_s(\Omega)$	$R_{ct}(k\Omega)$	$C_p(\mu F)$	OCP(V/SCE)
Al-6Si alloy	40.37	15.57	1.259	-0.8454

A large fluctuation in open circuit potential for the alloy was seen during the time of 100s exposure (Table1). After a period of exposure the OCP fluctuation decreased and reached steady state. The steady state OCP of the alloy is -0.8454V. The OCP values mainly depend on the chemical compositions and thermal history of the alloy.

Impedance measurements-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. a shows the Nyquist diagrams (suggested equivalent circuit model shown in Fig. 2) of the Al-6Si alloy in simulated seawater. 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.

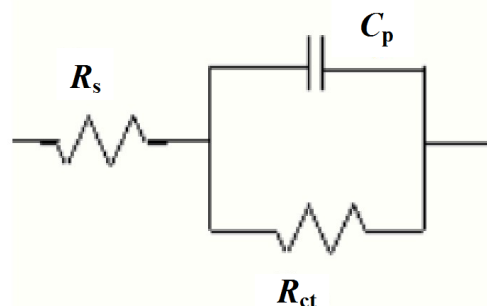


Fig. 2: Electrical equivalent circuit used for fitting of the impedance data of Al-6Si alloy in seawater

Fig.3.a shows the Nyquist diagrams (suggested equivalent circuit model shown in Fig.2) of the Al-6Si alloy in 0.1M NaCl in de-mineralized (DM) water. In Nyquist diagram, the imaginary component of the impedance (Z'') against real part (Z') is obtained in the form of capacitive-resistive semicircle for the sample.

Fig.3.b shows the experimental EIS results in Bode magnitude diagram for Al-6Si alloy. Bode plot 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. The solution resistance (R_s) of the alloy is 40.37Ω , which is very negligible with respect to R_{ct} and the electrolyte behaves as a good ionic conductor. For the Al-6Si alloy, the charge transfer resistance (R_{ct}) value in simulated seawater is $15.57k\Omega$, and this indicates the corrosion resistance of the alloy.

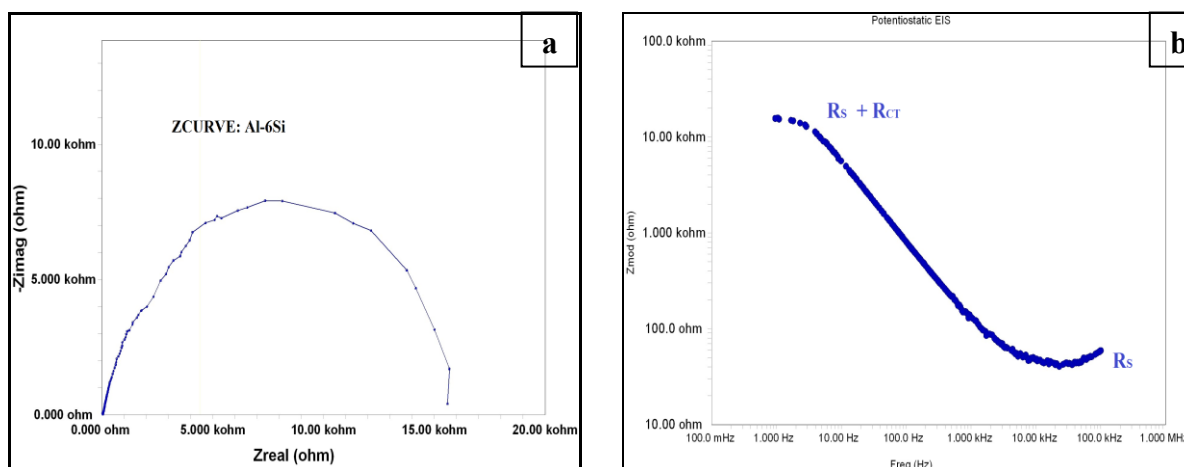


Fig. 3: (a) Nyquist plot and (b) Bode plot for Al-6S alloy in simulated seawater

Potentiodynamic Polarization Measurements

Table 2 shows the potentiodynamic polarization test results obtained from the electrochemical tests.

Table 2: Potentiodynamic polarization test results

Alloy code	$I_{corr}(\mu A)$	$E_{corr}(mV)$	$E_{pit}(mV)$	Corrosion rate(mpy)
Al-6Si alloy	6.300	-764	-480	5.287

A Potentiodynamic polarization curve of Al-6Si alloy in simulated seawater is shown in Fig. 4. The different intermetallic compounds can lead to the formation of micro-galvanic cells because of the difference of corrosion potential between intermetallics and α -aluminum matrix. The corrosion potential of Al-6Si alloy is $-764mV$ and Pitting potential (E_{pit}) is $-480mV$. The I_{corr} value, in simulated seawater is $6.3\mu A$, and the corresponding corrosion rate is $5.287mpy$.

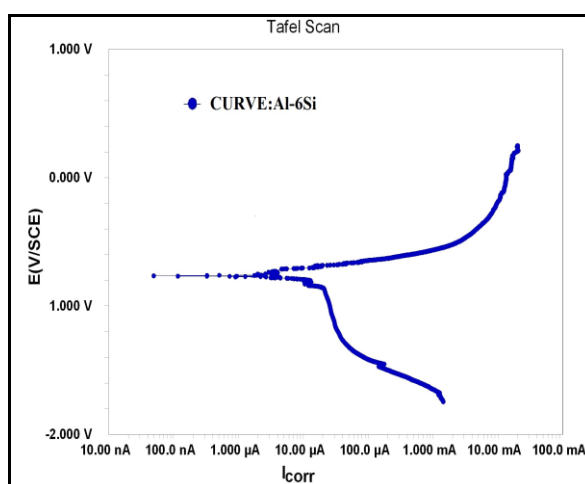


Fig. 4: Potentiodynamic polarization curves of peakaged Al-6Si alloy in simulated seawater

Microstructural Investigation

The microstructure of the selected as-corroded samples was observed under OLM and 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. The forms of corrosion in the studied Al-6Si alloy are not completely uniform and predominantly pitting corrosion as obtained by the OLM and SEM. Samples were characterized by OLM and SEM following potentiodynamic polarization tests. The peakaged Al-6Si alloy exhibited pits on their surface (Fig.5.a & Fig.5.b), which apparently had nucleated randomly. Conversely, the exposed surface of the alloy exhibited a corrosion product covering the surface after polarization. The optical micrographs (Fig 5.a) also showed that there was no corrosion in the fragmented and modified Al-Si eutectics.

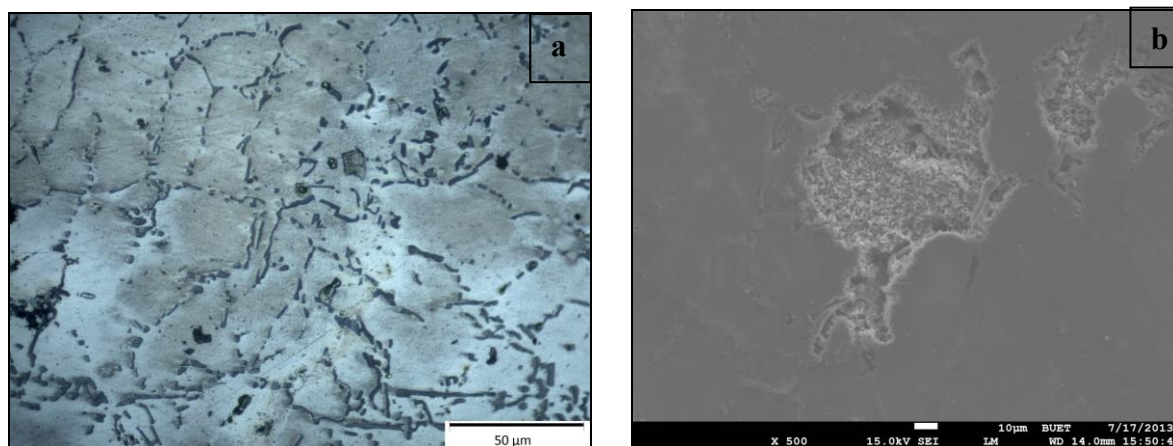


Fig. 5: (a) OLM and (b) SEM images show the damage surface morphology of as-corroded Al-6Si alloy in simulated seawater

CONCLUSION

The electrochemical impedance technique has been found to be appropriate to investigate the corrosion behavior of Al-Si hypoeutectic alloy in simulated seawater environment. The impedance results indicate the presence of a surface oxide and the polarisation results indicate this oxide to be at least partially permeable.

- ❖ From the EIS test, the solution resistance (R_s) of the alloy is 40.37Ω and this environment is a good ionic conductor. The R_{ct} value in simulated seawater is $15.57k\Omega$, corrosion resistance of the alloy.
- ❖ From the linear polarization and Tafel extrapolation plot, the I_{corr} value, in simulated seawater is $6.3\mu A$, and the corresponding corrosion rate is $5.287mpy$. In the anodic region, the Al-Si hypoeutectic alloy shows the lower corrosion resistant.
- ❖ Electrochemical results showed that simulated sea water is more accelerated the pitting corrosion. The forms of corrosion in the studied alloy are pitting corrosion as obtained from the OLM and SEM microstructures study with pits observations.

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