IJREAT International Journal of Research in Engineering & Advanced Technology, Volume 3, Issue 1, Feb-Mar, 2015
ISSN: 2320 – 8791 (Impact Factor: 1.479)
www.ijreat.org

Cyclic Polarization Analysis Of Corrosion Behavior Of 6061 Al/SiC$_p$ Composite With And Without Protective Coating

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Abstract

The present article deals with the investigations of effect of protective coating on the corrosion behavior of 6061 Al/SiC$_P$ composite in 3.5 M NaCl solution at high temperatures namely 40 ^{0}C and 50 ^{0}C using potentiodynamic polarization technique and cyclic polarization plots. The potentiodynamic polarization technique is used to determine the corrosion rate of the composite specimen with and without protective coating in the corrosion media. The cyclic polarization technique is used to study the pitting behavior of the composite with and without protective coating. The microstructure analysis is carried out using scanning electron microscopy (SEM).The results show that the peak aged composite is more prone to corrosion among the aged group of composites but when coated with aluminum shows a vast improvement in pitting nucleation resistance.

Key Words: *6061 Al/SiC, Cyclic Polarisation Technique, Aluminum coating.*

1. Introduction

Aluminum based metal matrix composites are among the traditional material which have been utilized for the construction ofship and submarine especially in weight sensitive applications [1–3]. Aluminum metalmatrix composites show attractive mechanical properties like high ratios of the Young modulus/density and yield strength/ density as well as the ability to retain strength at high temperatures; hence they lookvery promising and find applications in marine industries [4–5]. However, one of the main drawbacks ofaluminum matrix composites is the decrease in corrosion resistance compared to the base alloy. Various surface modification procedures are being evaluated forAl alloys and their composites to improve the oxidation and corrosion resistance. Many researchers are agreeing with the results stating that the major corrosion phenomena of aluminum based ceramic particle reinforced composite is pitting corrosion. One of the important tools of potentiodynamic polarization techniques to study the pitting corrosion behavior of composites is cyclic polarization analysis [6].

Cyclic Polarization (ASTM G 61) is a technique derived from Potentiodynamic polarization methods of corrosion analysis. It utilizes the anodic potentiostatic scan to study the corrosion phenomena until pitting is initiated, then the scan direction is reversed. The pitting tendency of a specimen in a corrosive medium is determined by the relative positions of the anodic and cathodic curves in cyclic polarization plot [7&8]. In electrochemical methods, the localized corrosion is studied by generating and analyzing the cyclic anodic polarization curves. The potential of the materials in the corrosive media is increased slowly using the potentiostat until a potential is reached at which the current increases rapidly due to the breakdown of passive film. Then the potential is reversed at a predetermined current density, to observe at what potential the localized corrosion stops. From this analysis it can be assumed that the natural corrosion potential in the selected corrosion media is less than the experimentally determined value. The cyclic polarization curve contains two parts corresponding to forward cycle and reverse cycle. The crossover point of these curves is known to be the protection potential. Due to the aforementioned advantages the cyclic polarization curves are commonly used to determine the localized corrosions of metal and alloys and the corrosion behavior of surface coatings [9&10].

This work concentrates in analyzing the corrosion behavior of the composite with and without aluminum coating as protective coating in 3.5 NaCl solutions at high temperatures namely 40 and 50 ^{0}C.

2. Experimental Work

2.1 Material

In the present work, 6061Al-15 volume percentage SiC composite material is under consideration. The composite is made of 6061Al alloy reinforced with particulate SiC (99.9% purity) and 28μm size. It was prepared by stir casting.

As cast composite cylinders were extruded with an extrusion ratio of 10:1.

2.2 Electrochemical testing

For electrochemical testing, solutionised, under aged, over aged and peak aged specimens of 3 cm length and 1.1 cm diameter are mounted in epoxy material. The specimens were polished with various grades of SiC paper, up to 1000 grade, wet polished to 3 µm grit with diamond paste and degreased just prior to immersion in 3.5 M NaCl solution room temperatures namely 303K during electrochemical testing.

Cylindrical coupons of length 1cm and 1.1 cm diameter were cut from peak aged composite rod and were coated by aluminum using DC magnetron sputtering technique. A magnetron sputter coating system was used to deposit Aluminum layer of thickness ~ 3.4 Microns (Determined by Gravimetric method) on the composite substrate at room temperature so that the coating procedure did not affect the temperature history of the specimen. A high-purity Al target (99.99%) with a diameter of 33 cm was mounted on the cathode, and argon was used as the bombardment gas. Prior to deposition the sputtering module was pumped down to a base pressure of 4 x 10 $^{-5}$ Pa. The sputtering pressure was set at 0.8 Pa. The target to substrate distance was 7.5 cm and the substrate was 10 x 10 x 3 mm 6061 Al/SiC composite. The power used for Al sputtering was set at 130 W. The sputtering was performed at room temperature for 180 minutes.

Similar experiments were carried out for the composite samples coated with aluminum. Thickness of the coating is around 3.4 microns (Gravimetric determination). For the electrochemical testing, the geometric area of the specimens exposed was 1 cm^2.

All solutions were prepared with distilled water and reagent grade chemicals. A solution volume of 500 mL was used for all tests. Electrochemical measurements were performed with a potentiostat under software control (CH Instrument, USA Model 604 A).

Polarization scans were initiated from -1100 mV versus SCE and scanned to approximately -200 mV, all potentials being relative to the open-circuit corrosion potential. Polarization curves recorded over the range – 1100 to -200 to mV, from which corrosion rates were estimated. All potentiodynamic scan rates were 0.33 mV/s. Electrochemical cell was composed of a three-neck glass flask, a large area platinum counter electrode, and saturated calomel electrode (SCE) as a reference electrode. All potentials are referenced to the SCE. Polarization resistance measurements were conducted via potentiodynamic polarization measurements.

The corrosion rate is obtained from the following expression [11]

$$CR(mpy) = \frac{0.129 x I_{CORR} x Eq.Wt}{D} \quad (1)$$

Where, I_{CORR}= Corrosion current density in µA/cm^2. Eq.Wt = Equivalent weight of the corroding specimen in gm.D = Density of the corroding species in g/cm^3.$I_{CORR}$is obtained by dividing the corrosion current (I_{CORR}) value by the area of specimen exposed to the electrolyte.

$$I_{CORR} = \frac{1}{2.3R}\left(\frac{\beta_a \beta_c}{\beta_a + \beta_c}\right) \quad (2)$$

Where,
R- Polarisation resistance (kΩ/cm^2)
β_a– Anodic slope (Volts/Decade);
β_c– Cathodic slope (Volts/Decade)

Also, the corrosion behavior of the composite coupons was determined electrochemically by cyclic potentiodynamic polarization, which is one of the promising techniques to measure the localized corrosion susceptibility. The solutions were heated to 50 ^{0}C and this temperature was maintained constant until the end of the tests. Before testing, the specimens were cleaned in an ultrasonic bath with distilled water and were left to dry. Then, they were placed in the polarization cell for 1 h beforeinitiating polarization. Polarization curves were obtained with a potential scan rate of 5 mV/ min by using a potentiostat.

3. Results and discussions

3.1 Corrosion behavior of 6061Al/SiC composite

Typical polarization curves for artificially aged 6061Al-based MMC containing 15 vol% SiC_p with and without aluminum coating in 3.5 M NaCl solution at 40 ^{0}C and 50 ^{0}Care shown in Fig 1 and 2. The corrosion characteristics are presented in table 2&3. The results of the polarization experiments carried out in 3.5 M NaCl solution at high temperatures, indicate that the polarization curves of solutionised, over aged and under aged composite samples shift towards the left with higher zero current potential (ZCP) and lower current densities (I_{CORR}) compare to the polarization curve of peak aged samples. This shows that there is an increase in corrosion rate for peak aged composite material even when the temperature is increased. This was in agreement with the results obtained by other authors for aluminum alloy particulate reinforced composites [12]. The effect of temperature is realized when the corrosion current densities were analyzed. Increase in temperature leads to increase in current density in the corrosion media and hence the corrosion rate.

Aluminum is more reactive by nature, but it has a good resistance to corrosion because of the formation of a passive oxide film. But aluminum is prone to galvanic corrosion when alloyed to more noble elements; this in turn leads to promotion of galvanic corrosion of the aluminum matrix in aluminum MMCs. The degree of galvanic corrosion depends on 1) the electrolyte to which it is exposed and 2) the reinforcement volume percentage. During fabrication of the composite there is a chance for micro structural change due to reinforcement/matrix reactions forming new inter metallic phase. Intermetallics can contribute to corrosion [13]. Also the effect of aging is realized when the shape of GP zones formed in the matrix is analyzed. This might be the reason for the peak aged composites aggressiveness in the chloride solution.

If the newly formed intermetallics are cathodic to the matrix, then severe corrosion will take place with respect to the matrix. Also the difference in coefficients of thermal expansion between the matrix and reinforcement generates higher dislocation density which in turn increases the corrosion rate. [14]. The aluminum coating as a protective coating efficiently decrease the corrosion rate of peak aged composite. This clearly visible when the corrosion current density of the coating in the corrosion media is compared with that of the peak aged composite at high temperatures. The pitting initiation nucleation can analyzed using the cyclic polarization technique.

Table 1 Corrosion characteristics of the artificially aged composite with and without aluminum coating in 3.5 M NaCl solution (aerated) at 40 ^{0}C.

Material	Corrosion potential (E_{CORR})	Polarization resistance (R_p)	Corrosion currentdensity (I_{CORR})	Corrosion rate
	mV Vs SCE	(kΩ/cm^2)	(µA/cm^2)	(Mils/year)
Solutionized	-726	7.63	6.87	3.17
Over aged	-750	5.78	7.19	3.32
Under aged	-780	4.24	7.35	3.4
Peak aged	-789	3.93	9.06	4.18
Aluminum coated peak aged	-711	11.4	4.88	2.25

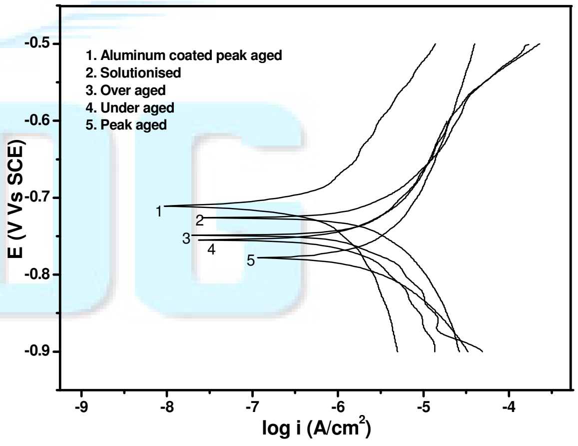

Fig 1 Potentiodynamic polarization curves of the artificially aged composite with and without aluminum coating in 3.5 M NaCl solution (aerated) at 40 ^{0}C.

Table 2 Corrosion characteristics of the artificially aged composite with and without aluminum coating in 3.5 M NaCl solution (aerated) at 50 ^{0}C.

Material	Corrosion potential (E $_{corr}$)	Polarization resistance (R_p)	Corrosion currentdensity (i_{corr})	Corrosion rate
	mV Vs SCE	(kΩ/cm^2)	(µA/cm^2)	(Mils/year)
Solutionized	-711	6.61	7.97	3.31
Over aged	-729	5.77	9.41	4.35
Under aged	-754	4.58	9.88	4.56
Peak aged	-778	3.45	10.2	4.71
Aluminum coated peak aged	-723	10.02	5.5	2.54

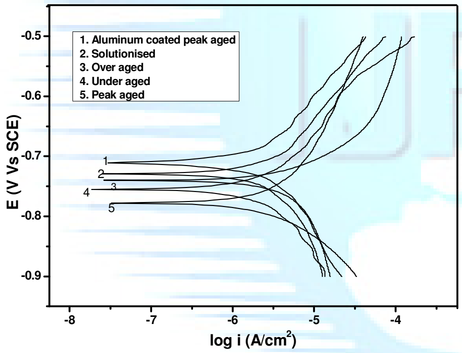

Fig 2 Potentiodynamic polarization curves of the artificially aged composite with and without aluminum coating in 3.5 M NaCl solution (aerated) at 50 ^{0}C.

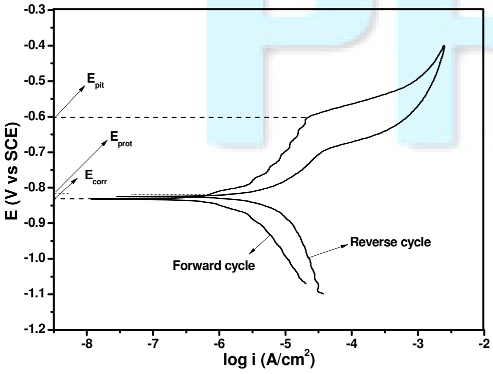

Fig 3 Cyclic polarization curve for the peak aged composite in 3.5 M NaCl (aerated) solution at 50 ^{0}C .

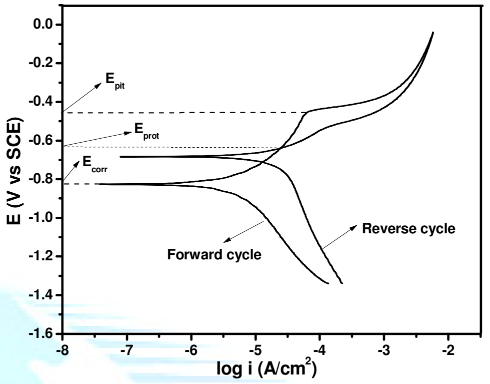

Fig 4Cyclic polarization curve for the aluminum coated peak aged composite in 3.5 M NaCl solution (aerated) at 50 ^{0}C .

Fig. 3&4 show the cyclic polarization curves of the peak aged composite with and without protective coating in 3.5 M NaCl solution at 50 ^{0}C. The curves contains two cycles namely forward cycle and reverse cycle. The open circuit potential (OCP) corresponds to the corrosion potential E_{CORR}. Another feature is the potential at which the anodic current increases drastically with applied potential (the breakdown potential). According to electrochemical theory, the nobler this potential is, the less susceptibility of the matrix is to the initiation of localized corrosion. The repassivation potential is the potential at which the "hysteresis" loop is plotted during the reverse scan. The "hysteresis", indicates that localized corrosion has occurred, such as pitting corrosion, and at the repassivation potential the initiated pits stop growing. Increase in current at an anodic potential may lead to oxygen evolution which in turn increases protective oxide layer thickness. Hence there observed a decrease in current at reverse scan.

From the cyclic polarization curves, it can be observed that both the polarization curves showed positive hysteresis as in the reverse anodic scan the current density was more than that for the forward scan. This implies that the pitting is the major form of corrosion in the composite when exposed to Chloride solutions. Also it is clearly visible that the hysteresis loop is smaller in the case of protective coating on the composite indicating the lesser degree of pitting corrosion when compared to that of the peak aged composite. Table3 demonstrates E_{CORR}, E_{PROT} and E_{PIT} obtained for the composite with and without protective coating in cyclic polarization technique. Significant difference wasobserved for E_{CORR} of both specimens when compared with each other. Generally, E_{CORR} value is indicative for the ionization tendency of materials in the selected corrosion media. The ionization tendency is decreased towards higher E_{CORR} values. The protective coating has higher E_{CORR} value when compared to that of the peak aged composite. This means the tendency for ionization is less in the case of the protective coating.

Table 3 Corrosion characteristics of peak aged composite with and without aluminum coating in 3.5 M NaCl solution at 50 ^{0}C (aerated).

Material	E_{CORR} (mV)	E_{PIT} (mV)	E_{PROT} (mV)	Pitting nucleation resistance E_{PIT} - E_{CORR} (mV)
Peak aged composite	-837	-619	-819	218
Aluminum coated peak aged composite	-814	-420	-616	394

E_{PIT} represents conservative measures of anodic pitting tendency because it corresponds to minimum potential below which pitting cannot be sustained. E_{PIT} value of the protective coating is higher when compared to that of the peak aged composite, indicating that the protective coating increases the upper limit of the potential below which pitting will not initiate. In electro chemical testing as per the general rule, pitting corrosion and crevice corrosion may be annihilated by keeping the electrode potential below to the protection potential. Protection potential is one below which the pitting initiation, crevice corrosion and crack initiation and propagation will not take place.

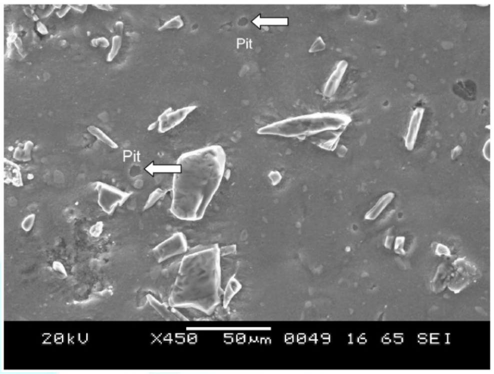

Fig.5 Microstructure of peak aged composite showing pits after exposure corrosion medium during the cyclic polarization test.

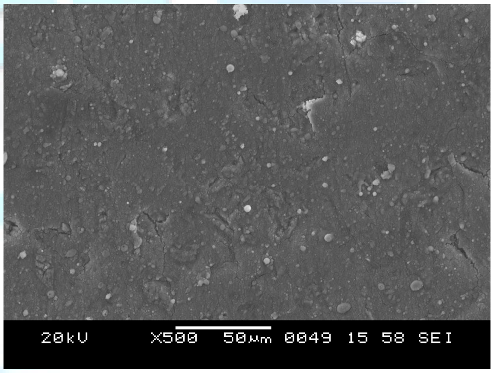

Fig.6 Microstructure of peak aged composite coated with aluminum after exposure corrosion medium during the cyclic polarization test.

As per the cyclic polarization analysis results, E_{PROT} of the protective coating falls at higher potential end when compared to that of the peak aged sample. This indicates the coating protects the composite specimen from pitting and crevice corrosion up to a potential of -616 mV. The pitting nucleation resistance of a specimen in a corrosive media represents the degree of pitting can occur in the same media. Higher the pitting nucleation resistance lower is the degree of pitting corrosion. The pitting nucleation resistance of the peak aged composite is almost doubled when it is coated with an uniform monolithic aluminum as protective coating. The protective coating effectively unexposed the alloying element precipitates, the interface regions and grain boundary regions of matrix. This in turn increases the pitting nucleation resistance of the composite to a large extent. This is clearly understood by analyzing the SEM micrographs of the peak aged composite with and without protective coating after the exposer to corrosion media during cyclic polarization analysis. The peak aged composite micrograph show more of pits when compared to that of the protective coating.

4. Conclusions

1. The results potentio dynamic polarization technique clearly suggests that the peak aged composite is prone corrosion in 3.5M NaCl solution at high temperatures. But the same when coated with aluminum as protective coating, the corrosion rate decreases to considerable extent.

2. Cyclic polariasation technique identifies that the pitting nucleation resistance of the peak aged composite is almost doubled when coated with aluminum in the 3.5M NaCl solution at high temperatures. The SEM analysis is in agreement with the polarization technique results. Hence it can be stated that Aluminum coating is beneficial in improving the corrosion resistance of the 6061Al/SiC composite in marine environment.

5.References

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