Research Article

Study of SiC/graphite particulates on the corrosion behavior of Al 6065 MMCs using tafel polarization and impedance

N. Sunitha[1] · K. G. Manjunatha[2] · Saifulla Khan[2] · M. Sravanthi[2]

Abstract
Aluminum metal matrix composites (MMC) have better mechanical properties than the alloy because of high strength-to-density ratios. In addition these composites exhibit low co-efficient of thermal expansion, high corrosion resistance. Al 6065 is the base metal selected for corrosion studies. Al 6065 MMCs are prepared by stir casting method. MMCs are prepared with reinforcement of particulates such as SiC and graphite. Composites are prepared by adding 2, 4 wt % of SiC particulates and hybrid composite with equal amount of SiC and graphite. Base metal alloy without adding any reinforcement is also casted in the same manner for comparison. Present research work involves the study of corrosion behavior of Al 6065 MMCs and the base metal alloy in different mediums using tafel polarization technique and Impedance. The corrosion medium used is 0.1 M acid chloride, 0.1 M acid sulphate and neutral chloride solution of 3.5%. The study is also compiled by SEM analysis of the corroded samples which depicts the deteriorated surfaces. Results indicate that Al 6065 hybrid composite is resistant towards corrosion because of its low percentage of graphite.

Keywords Al 6065 · Tafel polarization · Impedance · EIS · SEM

1 Introduction

The term "composite" broadly refers to a material system which is comprised of reinforcement distributed in matrix and which procure its distinguishing characteristics from the properties of its reinforcement, geometry and construction of the constituents and from the properties of the interfaces between different constituents [1]. Properties of MMCs strongly depend on the interfacial phenomena between the metal matrix and ceramic reinforcement [2–5]. The main cause of the corrosion in MMCs are reported as (a) galvanic coupling between the matrix and the reinforcement materials (b) formation of an interfacial phase between the reinforcement and matrix (c) micro structural changes processing contaminants resulted from manufacture of the MMC [6, 7]. Addition of low graphite percentages into pure aluminum was found to increase the corrosion of aluminum in 3.5% NaCl solution due to the activation effect for graphite towards the corrosion of aluminum [8, 9]. Chemical degradation of reinforcements and intermetallic phases cannot be detected by polarization techniques [10].

2 Experimental

2.1 Materials preparation

Al 6065 is selected as matrix material. Chemical composition of Al 6065 matrix material is given in the Table 1.

Aluminum ingots with 96.11 wt % commercial purity is used as matrix material which is procured from Fenfee Metallurgical. Reinforcement material used is micron sized SiC particles and graphite particulates. The method

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Table 1 Composition of Al6065 alloy (Wt %)

Element	Cu	Fe	Mg	Si	Zn	Ti	Bi	Zr	Cr	Mn	Al
% Composition	0.274	0.4	1.028	0.609	0.06	0.06	1.25	0.12	0.03	0.05	96.11

adopted is stir casting technique. Ingots are melted using electrical resistance furnace [11]. Matrix melt is stirred rigorously at a speed of 450 rpm and a vortex is created at the surface of the melt. Pre-heated, uncoated SiC particulates are introduced into the vortex. Composites containing 2, 4 wt % of SiC particulates and hybrid composite with equal amount of SiC and graphite are casted. In the same manner Al 6065 base metal alloy without any particulates is also casted for comparison. Molten melt is poured into steel moulds. Casted materials were cut into rectangular test coupons of length 6 cm, width 2.25 cm and thickness 4.95 mm using abrasive cutting wheel. Dimensions were measured using Vernier gauze. Rectangular specimens were grounded using different SiC grade emery papers like 80,100, 200,400 and 800. Before mounting for the electrochemical analysis the specimens were polished on polishing wheel using diamond paste to obtain a mirror finish by following standard metallographic techniques. Finally degreased in acetone and dried. Stock solutions of 0.1 M HCl and 0.1 M H_2SO_4 of analytical grade are prepared using distilled water. Similarly analytical grade NaCl solution of 3.5% concentration is also prepared using distilled water.

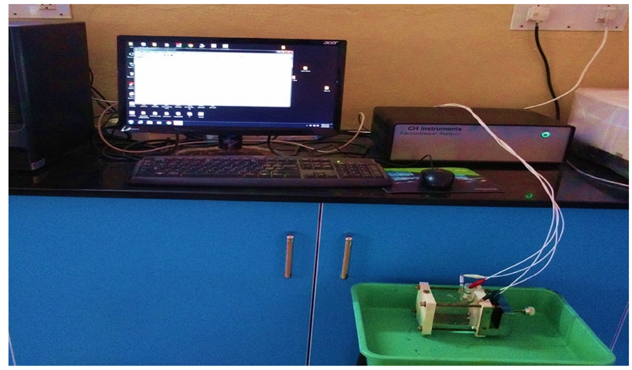

Fig. 1 Electrochemical work station of model 608 E-series

2.2 Electrochemical testing method

Electrochemical measurements are carried out using electrochemical work station of model 608 E-series procured from CH Instruments, USA having software version 12.04. Three electrode compartment cell made up of Pyrex glass with Ag/AgCl electrode (1 M KCl is filled) as reference electrode, platinum electrode as auxiliary electrode and rectangular Al 6065 specimen of 6 cm length, 2.25 cm width and 4.95 mm thickness used as working electrode for electrochemical measurements. Electrodes were placed in their respective positions in the electrochemical cell as shown in Fig. 1. This process is carried out at room temperature.

2.2.1 Tafel polarization

Polarization technique were used to obtain the micro cell corrosion rates [12]. Mirror finished surfaces of Al 6065 rectangular composites and the base metal alloy were allowed to come in contact with different concentrations of electrolytes like 0.1 M HCl, 0.1 M H_2SO_4 and 3.5% NaCl at room temperature. Specimens were in contact with the respective electrolyte solutions for 400 s to get steady open circuit potential (OCP). Polarization curves were recorded by polarizing the specimen to − 250 mV cathodically and + 250 mV anodically with respect to OCP at a scan rate of 1 mV/s.

2.2.2 Electrochemical impedance spectroscopy

Complex plane plots were obtained over a frequency range from 10^{-5} Hz to 1 MHz using an amplitude AC signal of 5 mV. At room temperature first open circuit potential of the working electrode is measured using different corrodents, later impedance measurements were carried out.

2.3 Scanning electron microscopy (SEM) analysis

Rectangular specimens of Al 6065 are grounded using SiC grade emery paper of grit size ranging from 80 to 800 as mentioned earlier and mirror finished. Specimens were subjected to electrochemical testing method and SEM micrographs were analyzed.

3 Results

3.1 Micro characteristics analysis

Micrographs depicts that in hybrid composite and in Al 6065 base metal alloy surfaces were less detoriated by the corrodents. As SiC is a semiconductor disintegration of matrix occurs at Al/SiC interface in the

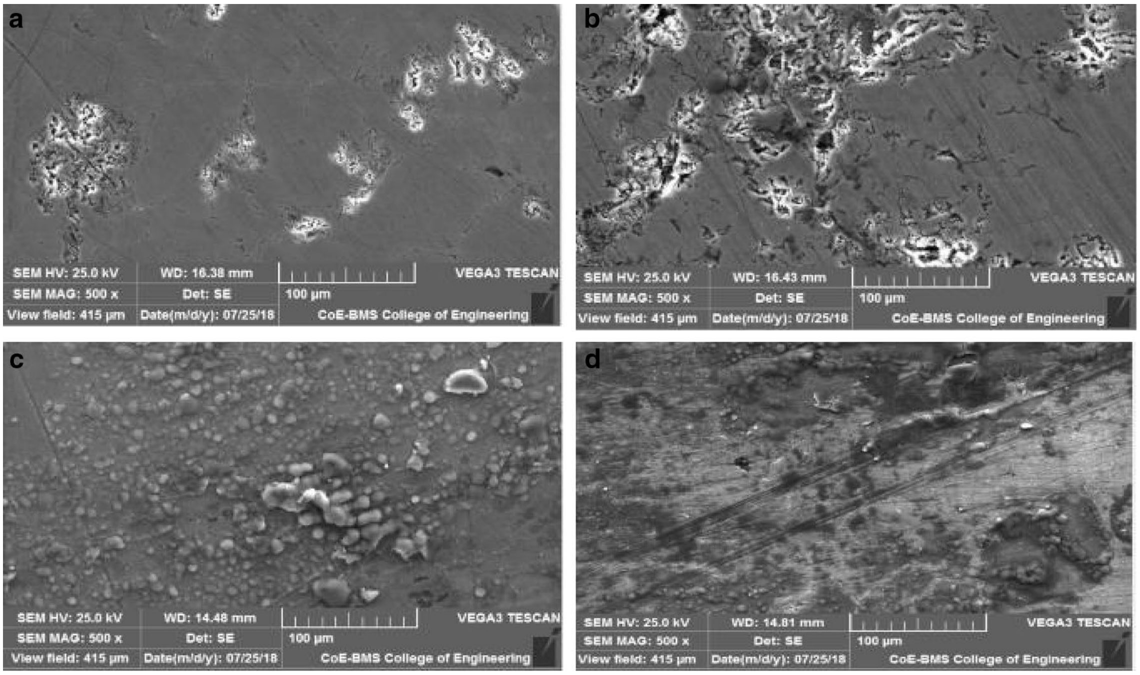

Fig. 2 SEM micrographs of polarized samples of Al 6065 base metal alloy, 2%, 4% and hybrid composites in 0.1 M HCl medium

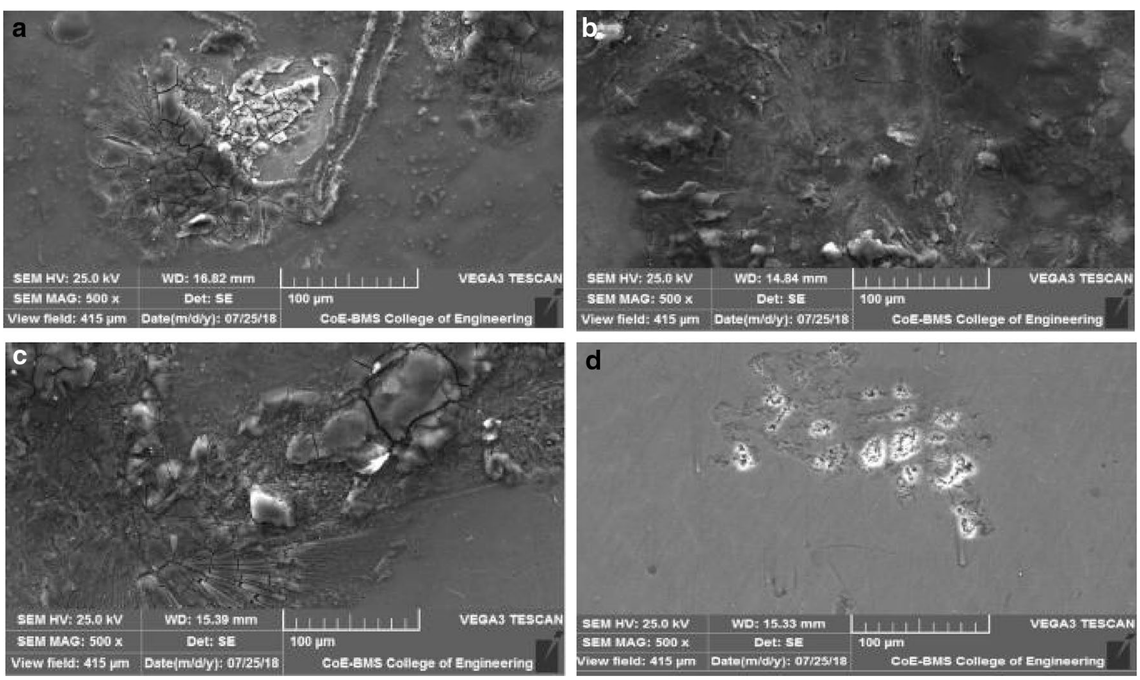

Fig. 3 SEM micrographs of polarized samples of Al 6065 base metal alloy, 2%, 4% and hybrid composites in 0.1 M H_2SO_4 medium

composites. Elemental composition of Al 6065 matrix and composites contains intermetallic precipitates like MnO_4 and $AlCu_3$ which increase the rate of corrosion in composites. SEM micrographs of as casted corroded samples of base metal alloy and its composites after electrochemical analysis in different electrolytes like 0.1 M HCl, 0.1 M H_2SO_4 and in 3.5% NaCl are shown in the Fig. 2, 3 and 4.

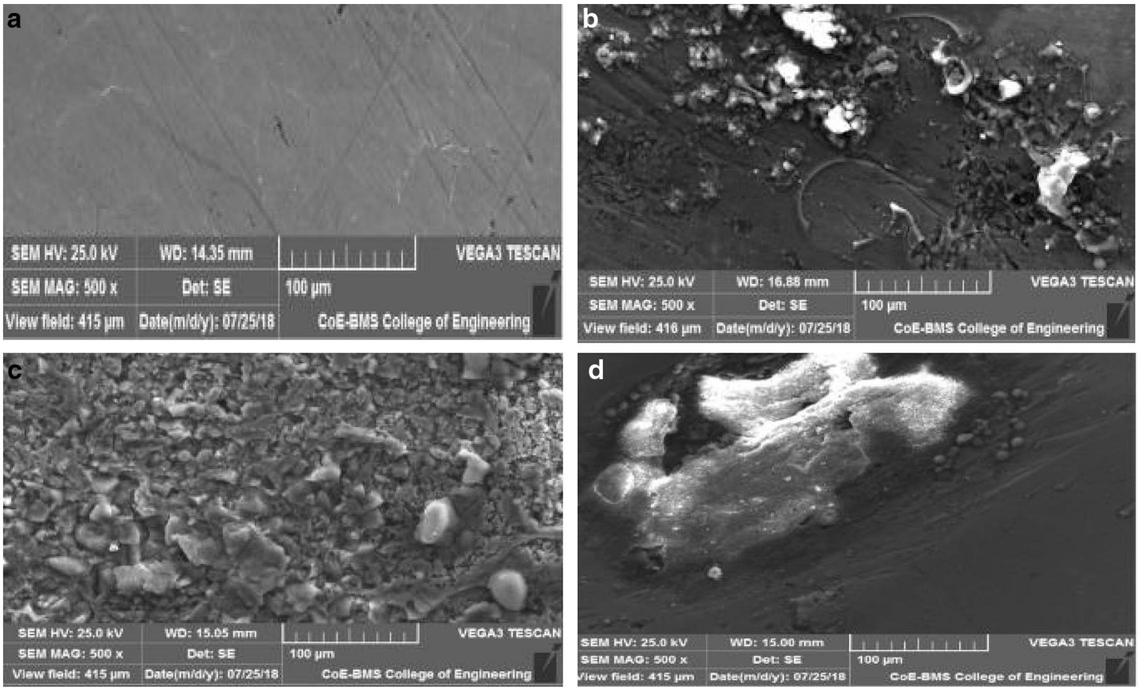

Fig. 4 SEM micrographs of polarized samples of Al 6065 base metal alloy, 2%, 4% and hybrid composites in 3.5% NaCl medium

Table 2 OCP of Al 6065 base metal alloy and its composites in various mediums

SiC Content	OCP (V) in different mediums		
	3.5% NaCl	0.1 M HCl	0.1 M H_2SO_4
0%	−0.5508	−0.6721	−0.6007
2%	−0.5608	−0.7068	−0.6286
4%	−0.5682	−0.7114	−0.6437
Hybrid	−0.5502	−0.6695	−0.5897

3.2 Electrochemical testing analysis

3.2.1 OCP measurements

OCP were recorded for Al 6065 composites and its base metal alloy in three different electrolyte solutions of 0.1 M HCl, 0.1 M H_2SO_4 and in 3.5% NaCl. Measured open circuit potentials are given in Table 2. The addition of SiC to the base metal alloy may have result in OCP to more positive, more negative depending on the alloy system, presence and absence of O_2 [13]. From the OCP values it is evident that with increase in % of SiC content in the composites potential shifts towards more negative values and corrosion rates increases, possibility of galvanic corrosion between SiC ceramic particles and Al 6065 matrix [14–18].

3.2.2 Tafel polarization curves

The logarithm of the current density as a function of potential has been taken to generate the polarization curves. In tafel extrapolation near the E_{corr} a linear region on both the anodic and cathodic legs has been observed. The slopes of the linear regions are taken as tafel constants named as β_a and β_c. E_{corr} is obtained by extrapolating these linear regions till they intersect [19]. Log I_{corr} values at the point of intersection of co-ordinates will give corrosion current density. Figure 5 are superimposed polarization curves of as casted Al 6065 base metal alloy and its composites in HCl, H_2SO_4 and in NaCl mediums. Whereas Fig. 6 shows tafel polarization curves of as casted specimens of Al 6065 alloy, 2%, 4% and hybrid composites in different mediums. From the tafel curves it is evident that hybrid composite have lower corrosion rate than compared with base metal alloy. As hybrid composite is casted having equal amounts of SiC and graphite, having low percentage of graphite in the hybrid metal matrix makes the composite better resistant to corrosion [20, 21]. Polarization curve of the hybrid composite shows lowest cathodic, anodic and I_{corr} currents and hence it is resistant to corrosion.

3.2.3 EIS measurements

Impedance spectrum shows large capacitive loop at high frequencies and an inductive loop at low frequencies [22].

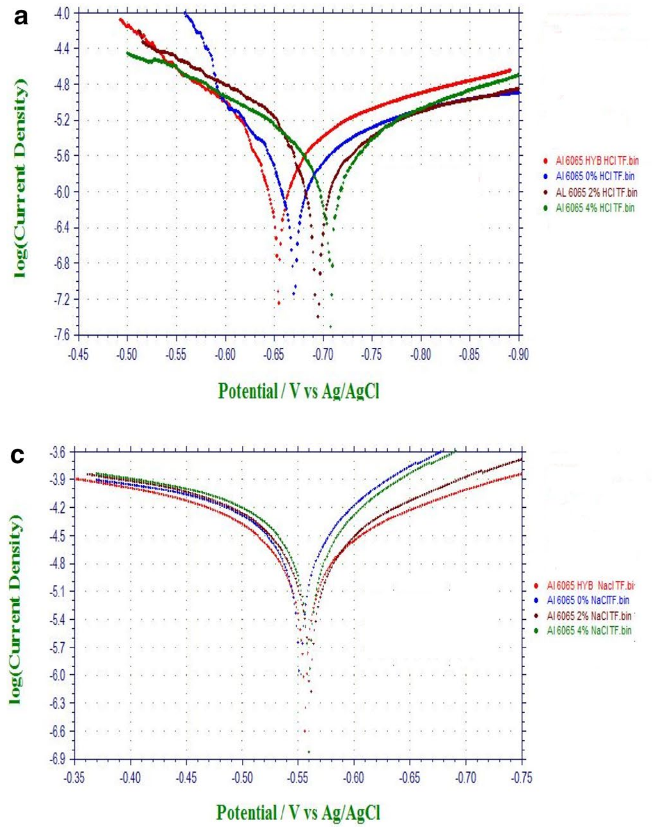

Fig. 5 Anodic-cathodic polarization curves of Al 6065 base metal alloy, 2%, 4% and hybrid composite in 0.1 M HCl, 0.1 M H_2SO_4 and 3.5% NaCl mediums

High frequency capacitive semicircle is associated with constant phase element (CPE) and while inductive loop is related with the roughness, inhomogeneities of the solid surface [23]. Diameter of the semicircle is large for hybrid composite in all the mediums [24, 25]. This increase in diameter of the semicircle for hybrid composite affirms that it is higher corrosion resistant [26]. Figure 7 shows complex plane plots obtained for Al 6065 and its composites in 0.1 M HCl, 0.1 M H_2SO_4, and 3.5% NaCl solutions.

3.2.4 Determination of corrosion rate (CR) using the equation

$$\text{CR (mpy)} = \frac{0.128 \times \text{Equivalent Weight} \times I_{\text{Corr}}}{D} \quad (1)$$

where mpy is mils penetration per year, I_{corr} is corrosion current density (μA cm^{-2}) & 'D' is density of the base metal alloy and its composites (g cm^{-3}). Table 3 Shows corrosion rates for Al 6065 base metal alloy and its composites in different mediums, calculated using the above Eq. (1) [27]. β_a, β_c represents anodic tafel slope and cathodic tafel slope whereas R_p represents linear polarization resistance (LPR). R_p, β_a, β_c, I_{corr} and corrosion rates which are tabulated in the Table 3 are obtained from the tafel extrapolation curve which is shown in Fig. 8. Corrosion order of the corrodents are NaCl < H_2SO_4 < HCl. Figure 9 shows R_p is more for hybrid composite in all the mediums which affirms the low corrosion rate of the specimen. It has been observed that corrosion current and corrosion rate increased with increase in percentage of SiC composition in Al 6065 matrix and whereas it is decreased in hybrid composite.

4 Discussion

4.1 Effect of NaCl medium on the corrosion

From Fig. 16 for 4% Al 6065 composite current decreases in the cathodic side and the cathodic reaction is hydrogen liberation and O_2 reduction.

$$2H^+ + 2e \rightarrow H_2$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$

After reaching I_{corr} and E_{corr} current in the anodic side increases due to aggressiveness of chloride ions.

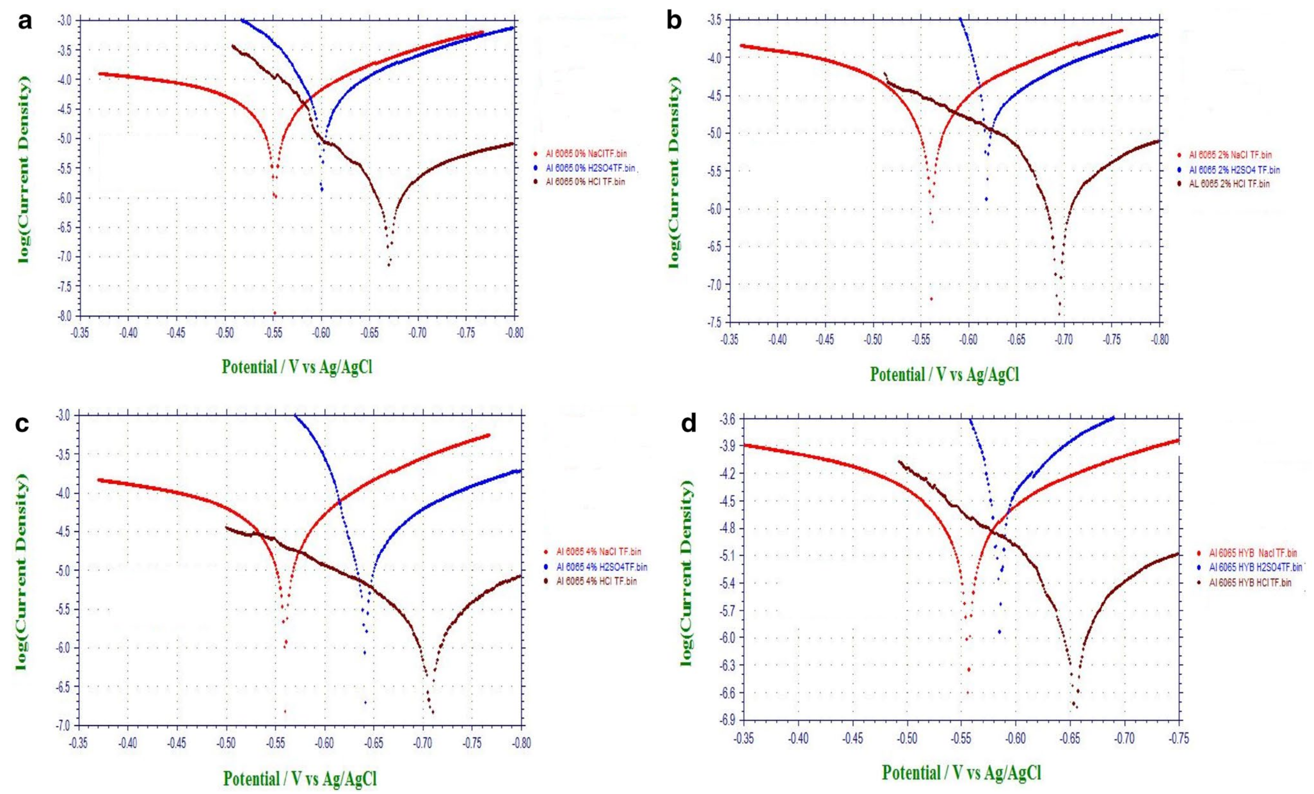

Fig. 6 Tafel polarization curves of Al 6065 base metal alloy, 2%, 4% and Hybrid composites in different mediums

$$Al \rightarrow Al^{3+} + 3e^-$$

$$Al^{3+} + 3Cl^- \rightarrow AlCl_3 + 3e^-$$

In the case of 2% composite anodic current decreases and E_{corr} shifted to more negative value. For 0% alloy E_{corr} shifted to more negative direction with the formation of Al_2O_3 layer.

$$Al + 3OH^- \rightarrow Al(OH)_3 + 3e^-$$

$$2\,Al(OH)_3 \rightarrow Al_2O_3 3H_2O$$

Hybrid composite shows lowest I_{corr} due to formation of oxide film and presence of low percentage of graphite particles being anodic to the matrix [8, 28, 29].

4.2 Effect of HCl medium on the corrosion

Using HCl as corroding medium, it is attributed that Cl^- ions are likely to percolate through the Al_2O_3 oxide film there by retarding the self-healing ability of the oxide layer on the metal surface. This results in the formation of intermediate soluble complex.

$$Al_{(S)} + nCl^- \rightarrow \left[AlCl_n\right]^{(n-3)} + 3e^-$$

This complex is the cause for the dissolution of the Aluminum ions from the lattice into the solution and leads to thinning of the passive layer on the metal surface and ultimately increasing the corrosion rate in the composites [30–32].

4.3 Effect of H_2SO_4 medium on the corrosion

SiC being cathodic to Al 6065 matrix, corrosion rate increases with increase in percentage of SiC due to breakdown of oxide film on the surface. Al_2O_3 layer becomes thin due to SO_4^{2-} ions and composites loses its passivation.

Protective Oxide layer formed on the surface of Al 6065 can be destroyed by the action of 0.1 M H_2SO_4.

$$4Al + nH_2O + 3O_2 \rightarrow 2Al_2O_3\left(H_2O\right)n$$

By the interaction of HSO_4^- anions with hydrated film of oxide, $Al_2[(SO_4)_3(H_2O)n]$ is formed.

$$Al_2O_3\left(H_2O\right)n + 3HSO_4^- + 3H^+ \leftrightarrow Al_2\left[\left(SO_4\right)_3\left(H_2O\right)n\right]_{ads} + 3H_2O$$

As the complex formed is soluble in aqueous medium, it can be desorbed from the surface leaving free active sites for the attack of anions like HSO_4^- or SO_4^{2-} [33, 34].

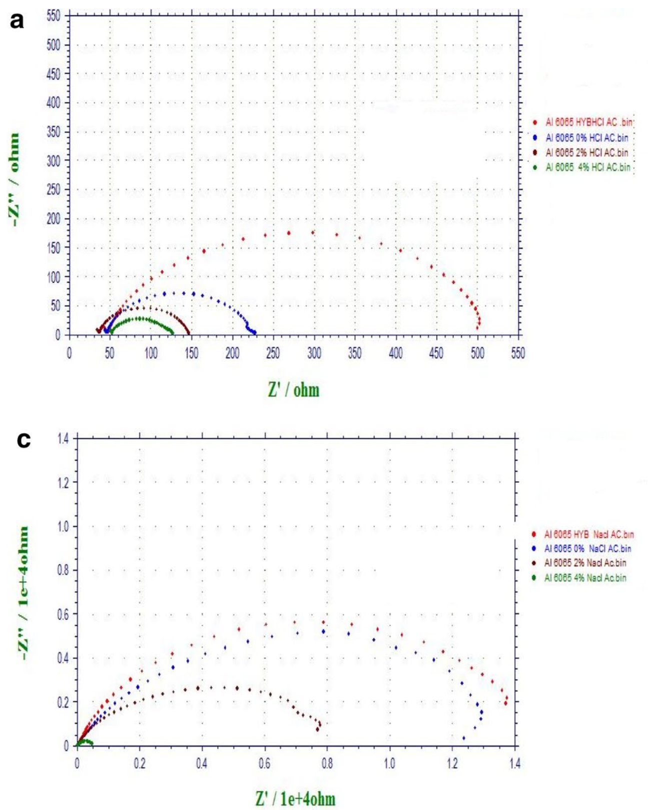

Fig. 7 Complex plane plots of Al 6065 alloy and its composites 2%, 4% and hybrid composites in 0.1 M HCl, 0.1 M H_2SO_4 and 3.5% NaCl mediums

Table 3 Corrosion rates, I_{corr}, R_p, β_a and β_c of Al 6065 base metal alloy and its composites in different mediums

Medium	% of SiC	R_p (Ohm)	I_{corr} (A cm^{-2}) $\times 10^{-6}$	β_a (V)	β_c (V)	CR (mpy) $\times 10^{-5}$
0.1 M HCl	0%	324	98.1	7.039	5.315	4.0107
	2%	313	103.9	7.600	6.331	4.2592
	4%	257	150.4	8.247	6.070	6.1832
	Hybrid	864	36.4	5.935	5.586	1.4977
0.1 M H_2SO_4	0%	888	44.85	3.644	5.163	1.8454
	2%	886	47.32	4.125	6.752	1.9345
	4%	859	48.72	4.314	6.896	1.9972
	Hybrid	1445	31.75	3.476	6.795	1.3053
3.5% NaCl	0%	11,666	3.787	5.824	3.649	0.1556
	2%	10,568	3.808	5.840	4.158	0.1566
	4%	10,104	3.992	7.714	3.632	0.1632
	Hybrid	12,569	3.728	5.034	4.982	0.1528

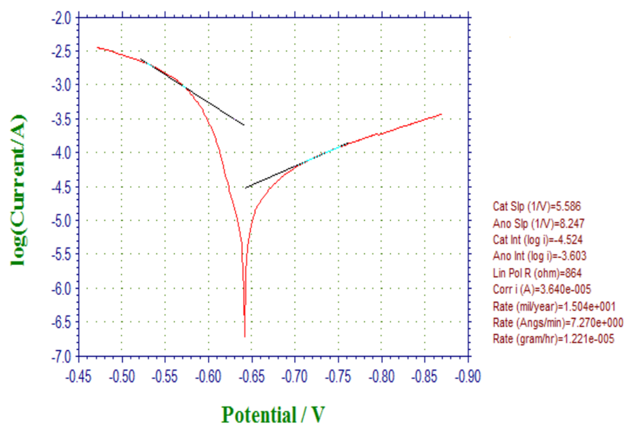

Fig. 8 Tafel extrapolation curve of Al 6065 hybrid composite using 0.1 M HCl medium

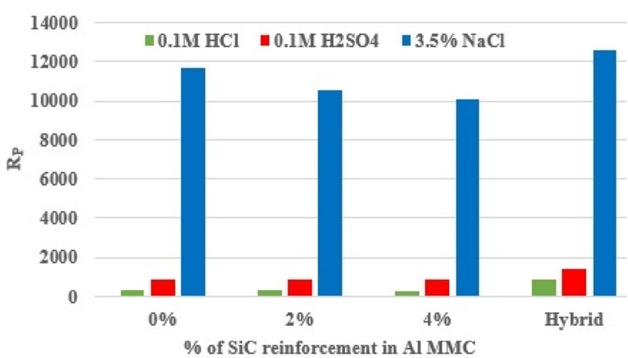

Fig. 9 R_p versus % of SiC reinforcement in the Al 6065 metal matrix using 0.1 M HCl, 0.1 M H_2SO_4 and 3.5% NaCl mediums

5 Conclusions

The effect of adding 2%, 4% SiC to the base metal alloy and hybrid composite with equal amount of SiC and graphite was investigated by polarization and EIS technique in different inorganic acids and neutral chloride media lead to the following conclusions:-

- Potentiodynamic polarization and impedance studies of the corrosion behavior of 6065 Al alloy and its composites showed that the corrosion resistance of the base metal alloy is greater than that of the composites [35].
- Corrosion rate of hybrid composite exhibited better corrosion resistance compared to the base metal alloy.
- Tafel curves shows I_{corr} and corrosion rate increased with increase in SiC content in the composites.
- Impedance spectra shows hybrid composite and base metal alloy exhibit better resistance towards corrosion as the diameter of the semicircle is large for hybrid followed by the base metal alloy.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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