

ABSTRACT

Silicon carbide particulate – reinforced Al6061 matrix alloy possess a unique combination of high specific strength, high elastic modulus, good wear resistance and good thermal stability than the corresponding non-reinforced matrix alloy system. They are used in aerospace, automobile and marine industries because of their increased corrosion resistance. In the present investigation, the corrosive behavior of Al6061-SiC particulate composites prepared by liquid metallurgy has been studied in acid chloride, acid sulphate and neutral chloride medium. Samples were prepared by taking different percentage of SiC and casted by liquid metallurgy and samples were prepared as per ASTM standard. In this paper the corrosion characteristics of as casted Al 6061/ SiC composites were experimentally assessed using Tafel extrapolation technique and A.C. Impedance or electrochemical impedance spectroscopy (EIS) technique. Polarization studies indicates an increase in corrosion resistance in composites compared to the metal matrix alloy. Tafel extrapolation technique and electrochemical impedance spectroscopy were in good agreement. It is observed that corrosion rate is more in acid chloride and acid sulphate media than in neutral chloride media. Further polarization curves indicates that corrosion rate decreases with the increase in the reinforcement content of the composite in as casted Al6061 composite. EIS study reveals that the polarization resistance (R_p) increase with increase in SiC content in composites, thus improved corrosion resistance in composites.

KEY WORDS: Al6061, Composite, SiC, Tafel, AC impedance, EIS.

1. INTRODUCTION

Most corrosion phenomena are of electrochemical nature and consist of reactions on the surface of the corroding metal. Therefore electrochemical tests methods can be used to characterize corrosion mechanisms and predict corrosion rates. Several techniques can be employed for evaluation and study of corrosion with reinforcement and among the most used are the electrochemical techniques. These techniques, besides analyze corrosion as a electrochemical phenomenon and therefore present greater reliability, have the advantage of being fast and not igniting serious damage to the structure at the time of application can be used both in the laboratory and in the field.

Electrochemical impedance spectroscopy is a recent tool in corrosion and solid state laboratories that is slowly making its way into the service environment as units are decreased in size and become portable. Impedance Spectroscopy is also called AC Impedance or just Impedance Spectroscopy. EIS is Exploit Faraday's Law to characterize a chemical process in terms of electrical measurements. Electrochemical impedances is the response of an electrochemical system (cell) to an applied potential. The frequency dependence of this impedance can reveal underlying chemical processes. In general the e commonly employed electrochemical techniques to measure corrosion rates are polarization and A.C impedance spectroscopy techniques. ..[1-2]

Aluminium metal matrix Composites (AMCs) have received considerable attention for military, automobile, aerospace and marine environment fields because of their low density, high strength and stiffness [3-6]. Further addition of ceramic reinforcement such as SiC, graphite, alluminium oxide and boron etc increases the better corrosion resistance than their base alloy. (U.Achutha kini,Prakash Shetty, s. Divakar Shetty.) Metzger and Fishmann reviewed and discuss the corrosion of boron composite suffered from interfacial attack due to crevice and galvanic corrosion [7]. Pitting was the primary type of attack on the silicon carbide composite and was associated with the silicon carbide particles. A.J .Trowsdale et al studied on the influence of SiC reinforcement

on the pitting behavior of Al1050 and found that a significant contribution to the increased pitting susceptibility arises from presence of voids and crevice at the reinforcement/ matrix interface [8]. A Comparative study of silicon carbide composite and corresponding matrices of alloys 2024, 5456 and 6061 were carried out and it was found that pitting susceptibility was same for the composite and the matrix alloy except for the 2024 alloy (Trzaskoma et al) [9]. Polarization behavior and pitting morphology differed between the composite and matrix of Al6061/ SiC alloy composite were studied and deduced that the formation of aluminium carbide during processing and not galvanic coupling lead to the marked corrosion susceptibility of this composite.(Aylor and Moran) [10]. A. C. Impedance or electrochemical impedance spectroscopy (EIS) used to examine the chemical passivation of Al6061 alloy and composite with SiC-graphite and found that cerium pretreatment of all deoxidized materials increased the time to pit initiation relative to that for untreated composite and alloy (Mansfeld et al) [11].

The present investigation was initiated to ascertain the analysis of corrosion behavior of Al6061 base alloy and composite with different percentage of reinforcement SiC and hybrid composite with graphite in various medium such as acid chloride, acid sulphate and neutral chloride medium by using Tafel extrapolation technique and A.C. Impedance or electrochemical impedance spectroscopy (EIS) [11-13].

2. EXPERIMENTAL PROCEDURE

2.1. Material selection

Material utilized for present study is Aluminium alloy 6061. Al6061 which exhibit excellent Casting properties and reasonable strength used as the base alloy with good strength, being suitable for mass production of light metal casting and its composition is given in the table.1.

Table.1: Percentage Composition of Al6061base alloy

Element	Mg	Si	Fe	Cu	Ti	Cr	Zn	Mn	other	Al
Percentage	0.8-1.2	0.4 – 0.8	Max. 0.7	0.15 – 0.40	Max. 0.15	0.04 - 0.35	Max. 0.25	Max. 0.15	0.05	95.85

2.2. Reinforcement

SiC of AR Grade used as reinforcement in the form of particulate of mean diameter 25 micron of 99.8 percent of purity.

2.3. Composite preparation

Liquid metallurgy route using vertex technique was employed to prepare the composite. The Al 6061 alloy ingots were charged into a gas –fired crucible furnace and heated to a temperature of 750°C above the liquid temperature of the alloy and the liquid alloy was then allowed to cool in the furnace to a semi solid state at a temperature of 600°C. The preheated Silicon carbide reinforcement of 2%, 4% and hybrid Composite with graphite was added. The composite slurry was then stirred using a mechanical stirrer at a speed of 300 rpm with graphite coated helical shaped arranged blades using hexachloro ethane or hexafluoro ethane as a degassing tablet to improve the distribution of SiC particles in the molten Al6061 alloy. After degassing, Scum and other impurities were removed. The molten composite was then cast in the steel moulds [14-16].

2.4. Specimen Preparation

Cast material was cut into 15X15mm cylindrical pieces using an abrasive cutting wheel for the test coupons samples. The matrix was also cast under identical condition as composites for comparison, for corrosion study by weight loss method and For Polarization studies, composites and pure alloy matrix were cut into rectangular species of length 83mm, 21mm length width and 4mm thickness. The exposed flat surface of the mounted part was polished with 240, 320, 400, 600,800and1000 grade emery papers and polished according to standard metallographic techniques and degreased in acetone and dried.

3. EXPERIMENTAL PROCEDURE

3.1. Evaluation of Corrosion rate by Polarizations Technique.

Polarisation is an extremely important corrosion parameter, which enables one to understand the corrosion rate processes. During electrochemical corrosion testing, two different approaches such as Control of current (i.e., corrosion rate) and Control of potential (i.e., the oxidizing power) are apparent and measuring the resulting current. In each case the potential of an electrode in a conducting medium is changed by the flow of current in the electrolytic cell. The two different techniques in measuring the corrosion rate are Linear Polarisation method and Tafel's extrapolation .[17-18]



3.2 Linear Polarisation method

Potentiodynamic polarization studies of an Al6061 base alloy and its composite have been carried out. A solution of 3.5 % of sodium chloride, 0.1M acid chloride solution and 0.1M acid sulphate solutions were prepared. An electrochemical cell with a three-electrode Pyrex glass configuration was used for electrochemical measurements. Al6061 matrix alloy and its SiC composites [2%SiC, 4%SiC & hybrid (SiC and graphite)] were used as a working electrode. A platinum electrode and a Ag/AgCl electrode used as counter and reference electrode respectively. Polarization scan was performed in the electropositive direction at a rate of 0.01V / sec. The open circuit potentials were recorded for Al6061 matrix alloy and its SiC composites in neutral chloride media, acid chloride media and acid sulphate media. The open circuit potentials, corrosion current density (I_{corr}) and the corrosion potential (E_{corr}) were determined for Al6061 matrix alloy and its SiC composites containing 2% SiC, 4%SiC & hybrid (2% SiC and 2% graphite) in neutral chloride media, acid chloride media and acid sulphate media using electrochemical workstation Instrument (Model: CHI608E). The corrosion rate were calculated using the following relation and recorded in the table.2.

$$\text{Corrosion rate (mpy)} = \frac{0.13 \times a \times I_{corr}}{D \times n}$$

Where

Mpy = milli-inches per year, I_{corr} = Corrosion current density (μAcm^2), a = Atomic weight

d = density of the corroding species, (g/cm^3). n = valency of metal sample

3.3. Evaluation of Corrosion rate by Tafel extrapolation method

The Tafel extrapolation method for determining corrosion rate was used by Wagner and Traud to verify the mixed-potential theory. This technique uses data obtained from cathodic and anodic polarization measurements. Terminologies in a polarization diagram, which is plotted potential vs log current density. The solid lines represent the net anodic and cathodic currents for each reaction, while the dashed lines represent the forward and backward parts of each reaction. The intersection of the dashed lines gives the open circuit corrosion potential, E_{corr} (when applied current density, $I_{appl}=0$) and the corrosion current density I_{corr} . The intersection of the dashed lines gives the reversible potential for the reaction and its exchange current density. The anodic polarisation curve is predominant at potentials more +ve (noble) than E_{corr} and cathodic polarisation curve is predominant at potentials more -ve (active) than E_{corr} . β_a and β_c are the Tafel slopes in anodic and cathodic reactions and the intersection gives corrosion exchange current density. The corrosion rate of the system is proportional to I_{corr} , which is determined by the intersection between the total reduction rate and the total oxidation rate. The metal sample is termed the working electrode and cathodic current is applied to it by means of an auxiliary electrode composed of inert material such as platinum. Current is measured by means of an ammeter. Tafel extrapolation and A.C. Impedance spectroscopy (EIS) and potential studies were carried out using electrochemical workstation Instrument (Model: CHI608E). Current is increased by reducing the value of the variable resistance R. the potential and current at various settings are simultaneously measured.[19-23]

4. RESULT AND DISCUSSION

The polarization resistance method measures the instantaneous corrosion rates as compared to other methods on which metal loss is measure over a finite period of time. Instantaneous means that each reading on the instrument can be translated directly into corrosion rate. The experiment can be completed in a matter of minutes and the small polarization from the corrosion potential do not disturb the system. This permits rapid rate measurements and can be used to monitor corrosion rate in various process streams. Tafel polarization curves for Al6061 matrix alloy and its composites containing 2, 4 and (hybrid SiC+graphite) % by weight of SiC particulates in different medium such as acid chloride, acid sulphate and neutral chloride medium are shown in figure 1-6. The evaluated electrochemical parameters (i_{corr}), linear polarization resistance (R_p), anodic tafel slope (β_a), cathodic tafel slope (β_c) and Corrosion rate in miles per year that is associated with the polarization measurement for the Al6061 matrix alloy and its composites are given in the table.3. The corrosion parameters, corrosion current density (I_{corr}) and corrosion rate were obtained from the tafel polarization measurements. The values of the corrosion potential and corrosion current were obtained from the extrapolation of anodic and cathodic tafel lines located next to the linearized current regions as shown in the figure 1-6. it can be observed from the tafel plot that corrosion current values and corrosion rate decreases with increase in SiC content in the composites. The conducting SiC particulate possibly forms microgalvanic couple with Al6061 matrix alloy and

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causes pitting corrosion. The decrease in corrosion rate observed in case of composites is due to decoupling between SiC particles and Al6061 due to decoupling of conducting SiC particles after the interfacial corrosion product, thus eliminating the galvanic effect between them [24-27].

Table.2: Corrosion rate calculated using equation for Al6061 matrix alloy and its composites in various medium

Medium	Percentage of SiC	I _{Corr} (µA)	Atomic mass (a)	Valency n	Density (g / cc)	Corrosion Rate (mpy)
0.1M acid chloride medium	0	1.995 X 10 ⁻⁴	26.981539	3	2.7	8.639 X 10 ⁻⁵
	2	1.511 X 10 ⁻⁴	26.981539	3	2.7296	6.472 X 10 ⁻⁵
	4	4.932 X 10 ⁻⁶	26.981539	3	2.7388	2.105 X 10 ⁻⁶
	hybrid	5.993 X 10 ⁻⁶	26.981539	3	2.7206	2.575 X 10 ⁻⁶
0.1M acid sulphate medium	0	1.974 X 10 ⁻⁴	26.981539	3	2.7	8.548 X 10 ⁻⁵
	2	1.453 X 10 ⁻⁴	26.981539	3	2.7296	6.223 X 10 ⁻⁵
	4	6.865 X 10 ⁻⁵	26.981539	3	2.7388	2.930 X 10 ⁻⁵
	hybrid	1.337 X 10 ⁻⁴	26.981539	3	2.7206	5.745 X 10 ⁻⁵
3.5 wt % of neutral chloride medium	0	1.995 X 10 ⁻⁴	26.981539	3	2.7	8.639 X 10 ⁻⁵
	2	1.659 X 10 ⁻⁴	26.981539	3	2.7296	7.106 X 10 ⁻⁵
	4	1.511 X 10 ⁻⁴	26.981539	3	2.7388	6.450 X 10 ⁻⁵
	hybrid	1.567 X 10 ⁻⁴	26.981539	3	2.7206	6.734 X 10 ⁻⁵

Table.3. Corrosion rate calculated using Tafel extrapolation technique for Al6061 matrix alloy and its composites in various medium

Medium	Percentage of SiC	R _p (ohm)	I _{Corr} (A)	β _a	β _c	Corrosion Rate(mpy)
0.1M acid chloride medium	0 %	211	1.995	6.110	4.214	8.431
	2 %	207	1.511	6.431	6.828	6.408
	4 %	4241	5.195	12.557	7.179	2.210
	hybrid	3910	5.923	11.042	7.729	2.539
0.1M acid sulphate medium	0 %	305	1.453	3.697	6.115	8.370
	2 %	212	1.974	3.864	6.537	6.141
	4 %	323	1.337	4.156	5.920	5.732
	hybrid	582	6.865	3.944	6.938	2.920
3.5 wt % of neutral chloride medium	0 %	211	1.995	6.110	4.214	8.431
	2 %	12566	1.659	15.231	5.620	7.036
	4 %	217	1.511	6.828	6.431	6.382
	hybrid	99748	1.567	22.011	5.808	6.716

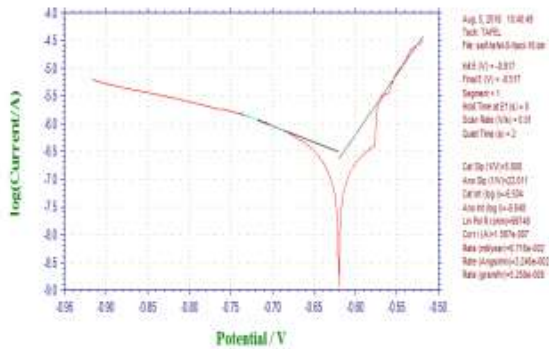


Fig 1. (a)

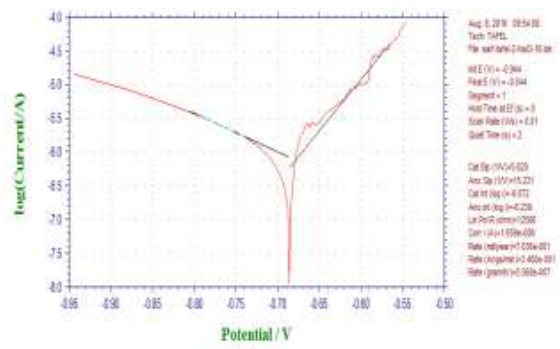


Fig 1. (b)

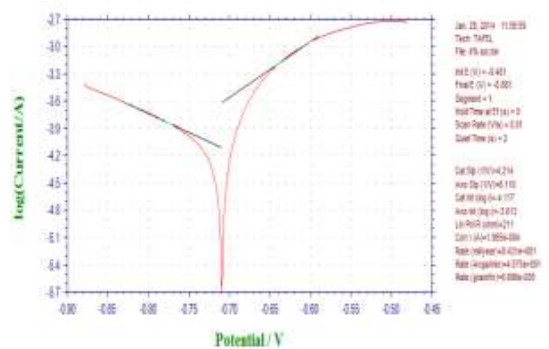


Fig 1. (c)

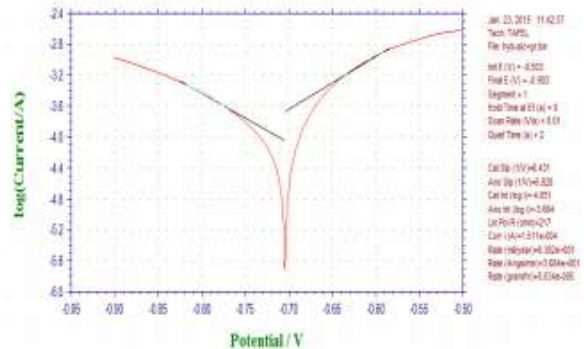


Fig 1. (d)

Figure.1 (a),(b),(c) and (d) Tafel extrapolation plots for A16061 matrix alloy and its composites in neutral chloride medium

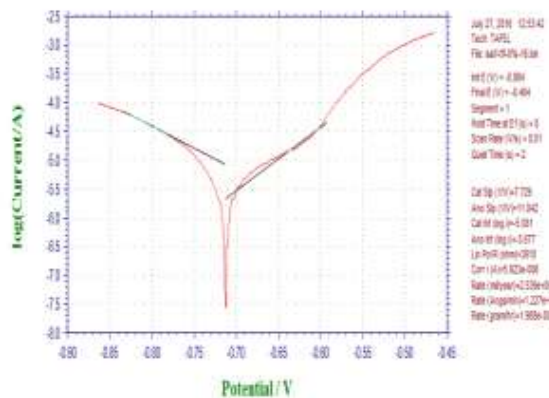


Fig 2. (a)

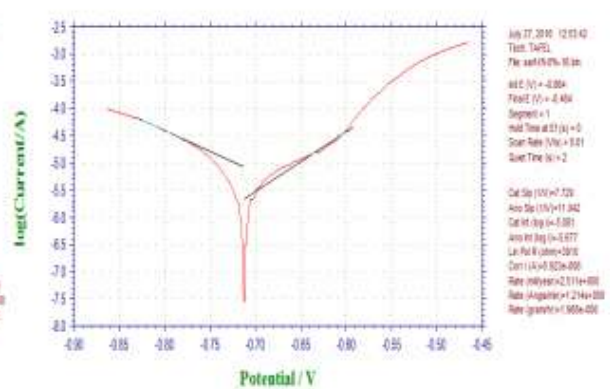


Fig 2. (b)

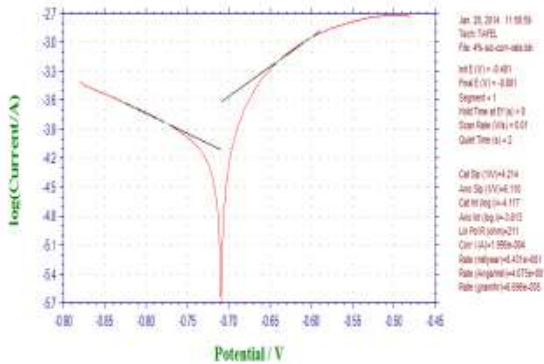


Fig 2. (c)

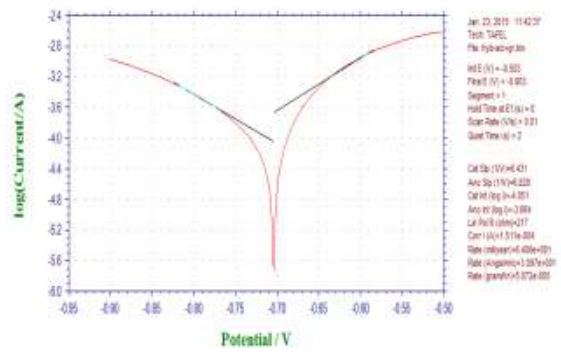


Fig 2. (d)

Figure.2. (a), (b), (c) and (d) Tafel extrapolation plots for Al6061 matrix alloy and its composites in acid chloride medium

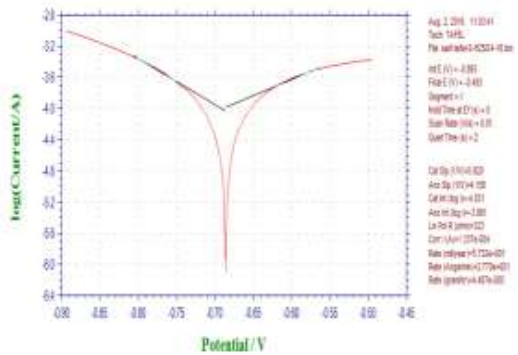


Fig 3. (a)

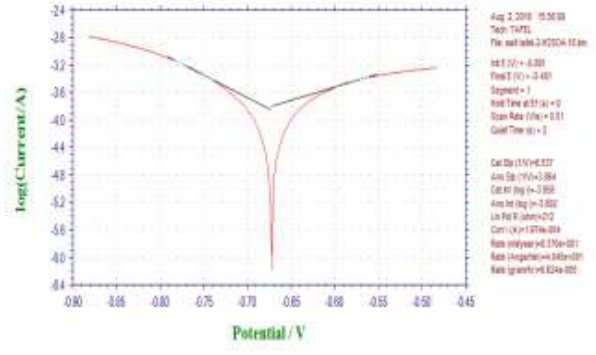


Fig 3. (b)

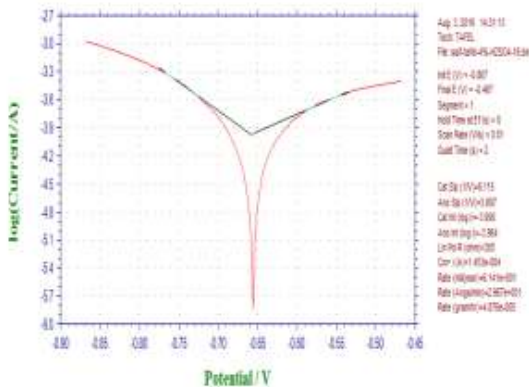


Fig 3. (c)

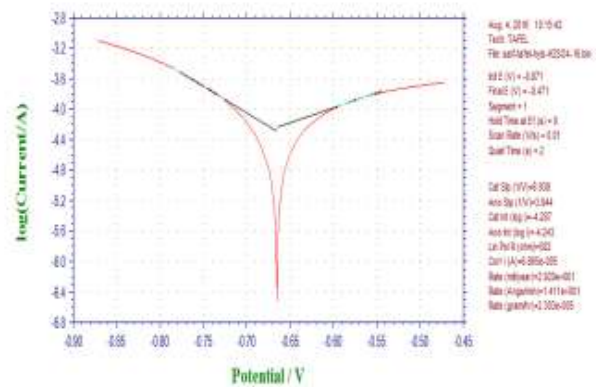


Fig 3. (d)

Figure.3.(a), (b),(c) and (d) Tafel extrapolation plots for Al6061 matrix alloy and its composites in acid sulphate medium

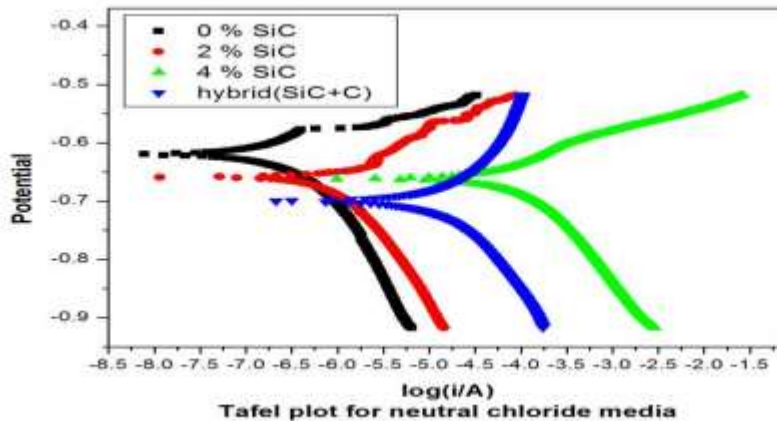


Figure 4: Tafel polarization plots for Al6061 matrix alloy and its SiC (2,4 & hybrid) composite in neutral chloride medium

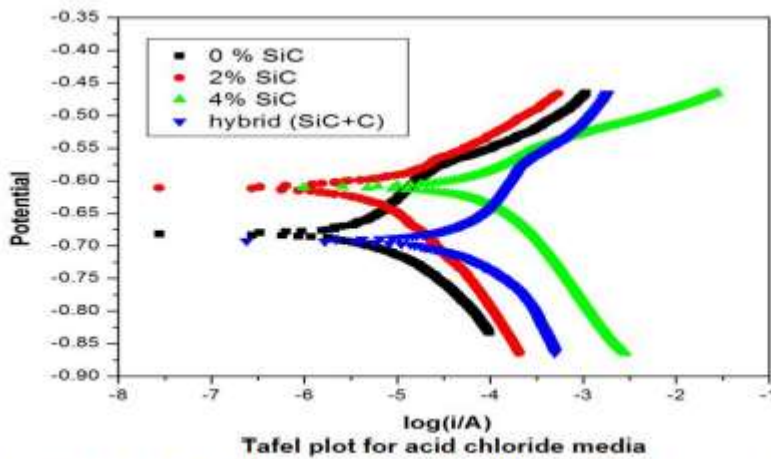


Figure.5: Tafel polarization plots for Al6061 matrix alloy and its SiC (2,4 & hybrid) composite in acid chloride medium

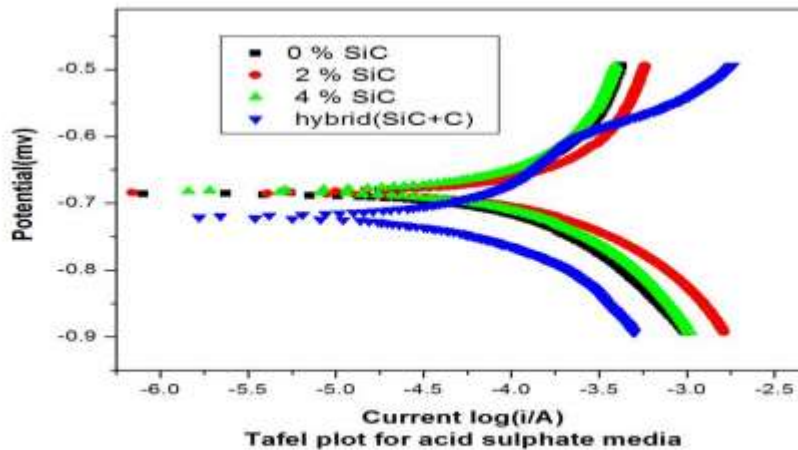


Figure.6: Tafel polarization plots for Al6061 matrix alloy and its SiC (2,4 & hybrid) composite in acid sulphate medium

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5. EIS STUDIES

EIS study of the matrix alloy and its composite is carried out at OCP in order to assess the contribution of the composites. Nyquist plots and its equivalent circuit used to fit the experimental data of Al6061 matrix alloy and its composites are shown in the figure.7-9. It can be observed from the Nyquist plots that radius of the capacitive loops above the real axis increased with increase in SiC content for the composites. Nyquist plot is also known as Cole-Cole plot or a complex impedance plane diagram. The imaginary component of impedance (Z'') is plotted against the real component of impedance (Z') at each excitation frequency. This plot could be used to compute the values of the uncompensated resistance between the working electrode and the reference electrode, R_u , the polarization resistance at the electrode/solution interface, R_p , and double layer capacitance at this interface, C_d . Knowledge of R_p permits the calculation of electrochemical corrosion reaction rates. It is clear that at high frequencies only the uncompensated resistance contributes to the real portion of impedance, while at very low frequencies the polarization resistance also contributes to this measurement. Once the excitation waveform becomes much faster than the charge-transfer rate, the polarization resistance becomes transparent to the technique. Experimental results obtained with a system for automatic recording and analysis of impedance data are given for a sample cell which represents a corroding electrode.

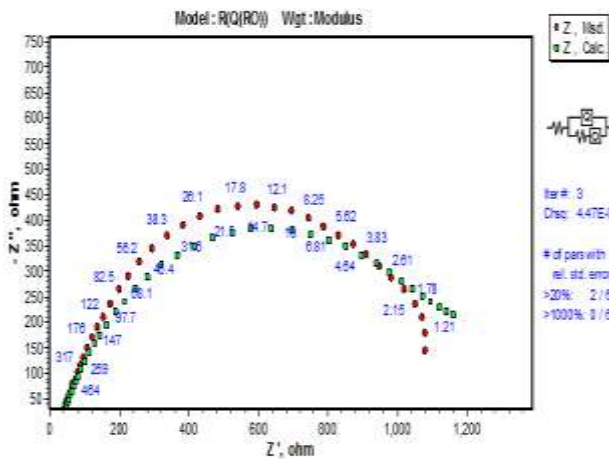


Fig 7. (a)

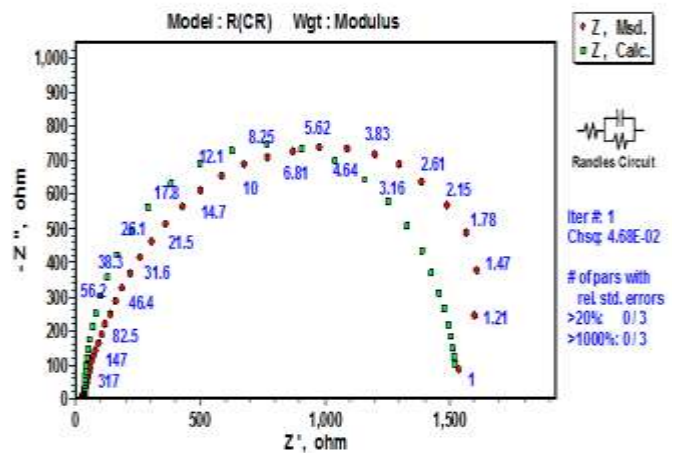


Fig 7. (b)

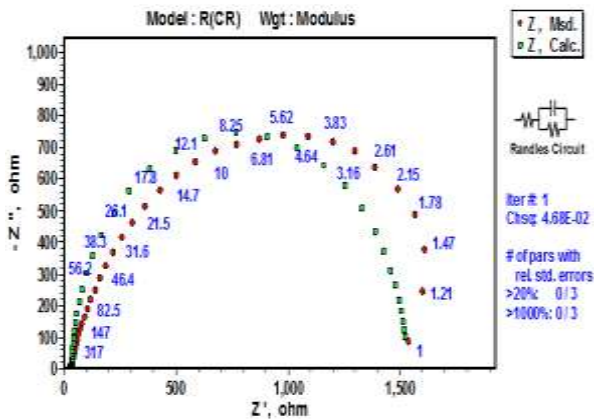
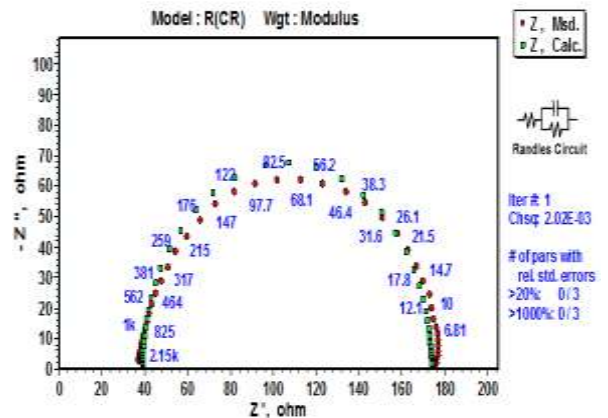


Fig 7. (c)

Fig 7. (d)



Figure

7 (a), (b), (c) & (d): Nyquist plot with Equivalent circuit model used to fit experimental data of Al6061 matrix alloy and its composites (2, 4 and hybrid) in neutral chloride medium

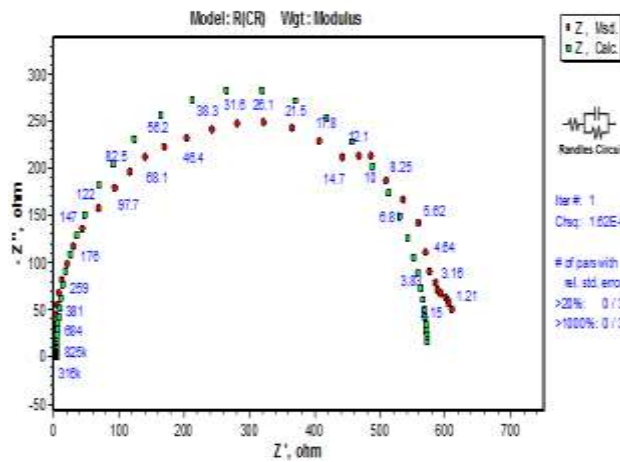


Fig 8. (a)

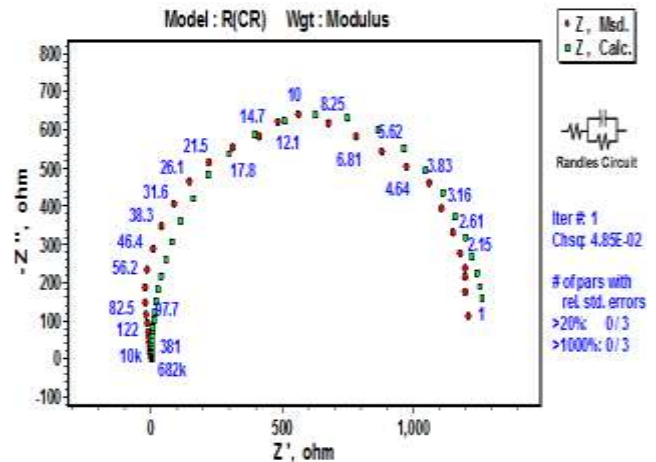


Fig 8. (b)

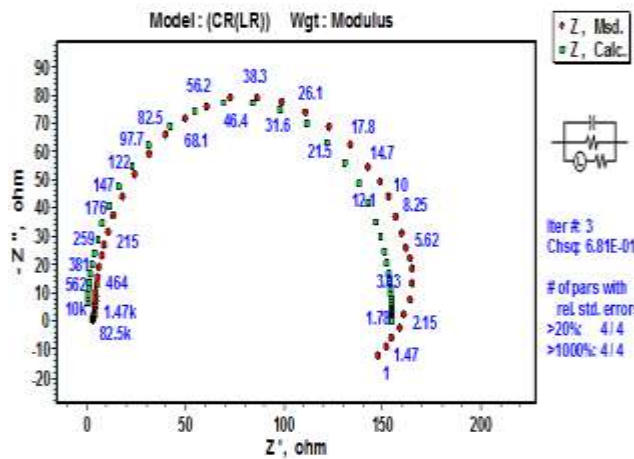


Fig 8. (c)

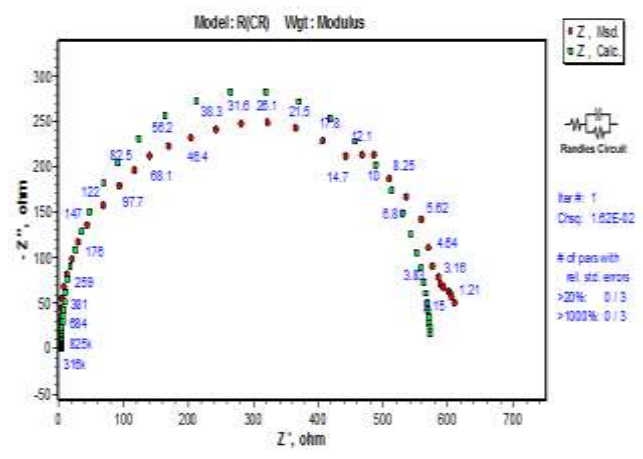


Fig 8. (d)

Figure 8 (a), (b), (c) & (d): Nyquist plot with Equivalent circuit model used to fit experimental data of Al6061 matrix alloy and its composites (2, 4 and hybrid) in acid chloride medium

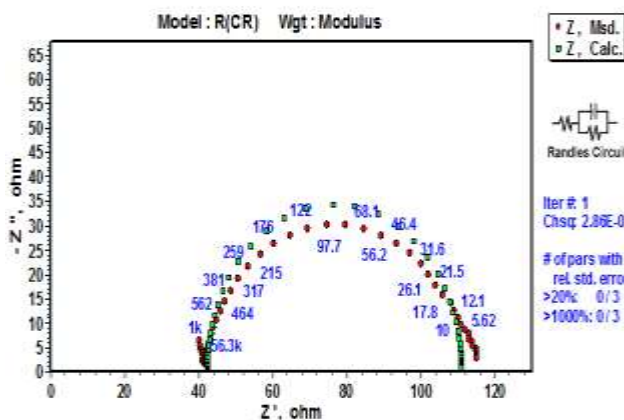


Fig 9. (a)

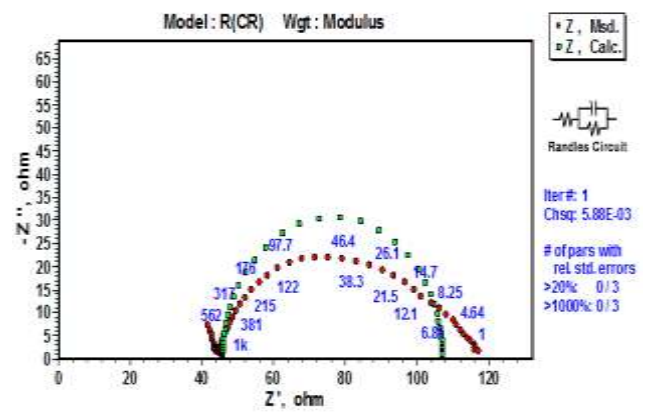


Fig 9. (b)

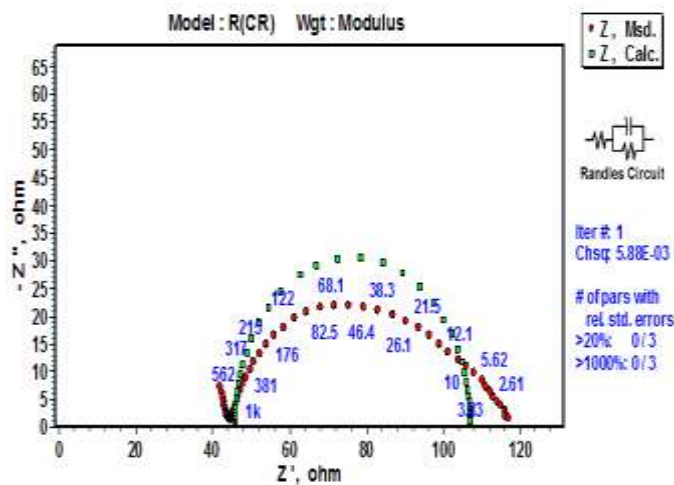


Fig 9. (c)

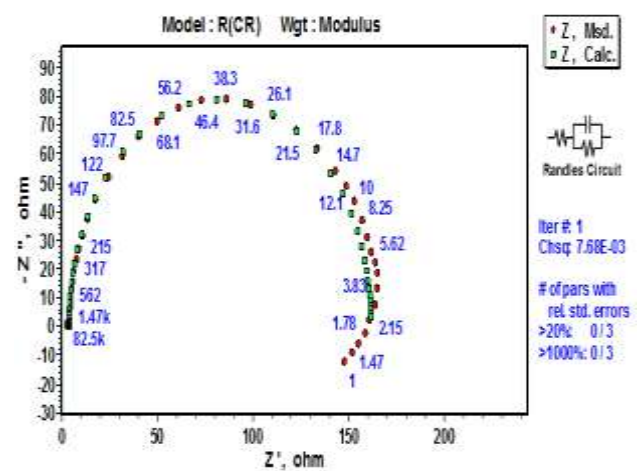


Fig 9. (d)

Figure 9 (a), (b), (c) & (d): Nyquist plot with Equivalent circuit model used to fit experimental data of Al6061 matrix alloy and its composites (2, 4 and hybrid) in acid sulphate medium

7. CONCLUSION

In this paper the corrosion characteristics of as casted Al 6061 matrix alloy and its composite with SiC (2% 4% and hybrid) were experimentally assessed using Tafel extrapolation technique and A.C. Impedance or electrochemical impedance spectroscopy (EIS) technique. Electrochemical corrosion rate measurements may be used to measure the corrosion rate of structures that cannot be visually inspected or subjected to weight loss tests.

From the result it is observed that Al6061 composite exhibited excellent Corrosion resistance in neutral chloride medium than in acid chloride and acid sulphate medium. The Corrosion rate of the composites was lower than that of the corresponding matrix alloy.

The Corrosion rate of composites decreases with increase in percentage of reinforcement which may be due to increase in bonding strength.

Increased corrosion resistance in composites is believed to be due to reinforcement particulate modifying the microstructure of matrix and also acting as physical barrier to the initiation and development of pitting corrosion.

8. ACKNOWLEDGEMENT

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REFERENCES

- [1] Recording and Analysis of AC Impedance Data for Corrosion Studies. Publications/274572947
- [2]. Use of Electrochemical Impedance Spectroscopy (EIS) to monitoring the corrosion of reinforced concrete
D.V. RIBEIRO, C.A.C. SOUZA, J.C.C. ABRANTES
- [3]. T.S.Srivastav , T. S . Sudarshan and G.e.Bobeck, Brit. Corr. J., 25(1990)39
- [4]. D.M.Aylor "HandBook" 9th edition .Vol13(American Society for metals.1987 p-859
- [5]. Sahin Y & Acilar M Composite Part A,24(2005)709
- [6]. W.Neil C. Garrard corrosion science, vol.36.No 5,pp837-851,1994. Elsevier Ltd
- [7]. M. Metzger and S. G. Fishmann, Ind.Engg.Chem. Prod.Res,Dev.22,296-1983
- [8]. A.J,Trowsdale.B.Noble, Sj,Haris . corrosion science,vol.38.No.2 PP.177-191.1996
- [9]. P. P .Trzaskoma , e.mc Cafferty and C.R. Crowe, j. electrochemical soc .130,(1983)
- [10]. D.M. Aylor and P.J.Moran j. electrochemical soc .132, 1277 (1989)
- [11]. F.Mansfeld, S. Lin. S. Kim and H.Shih Corrosion 45,615 (1989)
- [12]. U.Achutha et al Indian journal of Chemical technology vol.18.November 2011,pp,439-445



- K.Prasad rao and H.MD.roshan INCAL-9 . july1991
- [13]. M.S.N.Bhat, M.K. Surappa and H.V. Sudhaker nayak journal of material science 2(1991) 4991-4996
- [14]. Griffiths W N C 1994 Corrosion sci.36.837
- [15]. Ruses S , Venhoff H. sripta Metal mater. 1990:24:1021-1026
- [16]. Min K S, Ardell, Ek sj et al . j mater Sci.1995:30:5479-5483
- [17]. K.K. Alaneme and M.O. Bodunrin journal of Minerals & Material Characterization &Engineering, 12,PP,1153- 1165,2011
- [18]. Krupakara, P. V, Corrosion Characterization of Al6061/RedMud Metal Matrix Composites, Portugaliae ElectrochimicaActa 31(3), (2013), 157-164
- [19] N. Perez, Electrochemistry and Corrosion Science, Kluver Academic Press, Boston (2004).
- [20] A. J. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2 nd ed., John Wiley & Sons, New York (2001).
- [21] P. R. Roberge, Handbook of Corrosion Engineering, McGraw-Hill, NewYork (2000).
- [22]J. Koryta,J.Dvorak and Kavan, Principles of Electrochemistry, 2 ed., John Wiley & Sons, Chichester 1993).
- [23] C. A. A. Brett and A. M. O. Brett, Electrochemistry: Principles, Methods and nd applications, 2 ed., Oxford University press, England (1994)
- [24].H.C. Ananda murthy, V Bheema raju and C Shivkumara Bull. Mater Sci, vol,36, No,6, November 2013, PP1057-1066
- [25]. G.Velayudham, INCAL, 31 july-2 aug.1991, 879-882
- [26]. Z.Karm july-December 2014 vol.8 No.2 ISSN: 1985-3157
- [27]. El-Sayed M. Sherif, .A.Almajid, Fahamsyah Hamdan Latif, Harri Junaedi.Int j.Electrochem. Sci,6(2011)1085-1099