

Electroanalytical Study on the Corrosion Behaviour of TiO₂ Particulate Reinforced Al 6061 Composites

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ABSTRACT

Aluminium matrix composites reinforced with ceramic particulates, have significant applications in the field of aerospace, marine, automobiles, sports and recreation. In the present investigation, the corrosion behaviour of Al 6061-TiO₂ particulate composites prepared by liquid metallurgy, has been studied in chloride, nitrate and sulphate media using electroanalytical techniques such as Tafel, Cyclic polarization and Impedance (EIS) measurements. Surface morphology of the sample electrodes was examined using Scanning electron micrography (SEM) and Energy dispersive x-ray (EDX) analysis methods. To confirm the inclusion of TiO₂ particulates in the matrix alloy and identify the alloying elements and intermetallic compounds in the Al 6061 composites, XRD technique was used. The polarization studies indicate an increase in the corrosion resistance in composites compared to the matrix alloy. The results from all the media studied indicates that the relative degree of corrosion follows the order $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. The EIS study reveal that the polarisation resistance (R_p) increase with increase in TiO₂ content in composites confirming improved corrosion resistance in composites. The observed increase in corrosion resistance of TiO₂ particulate reinforced composites is believed to be due to the action of TiO₂ as physical barrier to the initiation and development of pitting corrosion, modifying the microstructure of matrix. The intermetallic phases AlFeSi rich and Mg₂Si formed, being conductive act as anodic to Al matrix and become the preferable sites for initial localised attack thus causing pits.

Key words: Al6061 Composites; TiO₂ particulates; Polarisation; SEM; Corrosion resistance.

INTRODUCTION

Particulate reinforced aluminium metal matrix composites (Al MMCs) and other aluminium based materials having huge applications in diverse fields such as light weight automotive structures, forgings for suspension, chassis, as well as advanced automotive components are exposed to a wide variety of corroding environment. Alloys of Al reinforced with ceramic oxides, carbides, nitrides and mineral silicate particulates possess attractive characteristics such as high specific modulus, high specific strength, low thermal expansion coefficient, light weight and low cost¹⁻³ and superior corrosion resistance.

Studies on Aluminium alloys reinforced with SiC⁴, B⁵, Al₂O₃⁶, TiC⁷, and ZrB₂⁸ report lower corrosion resistance for the composites compared to matrix alloys, owing to galvanic corrosion. On the other hand, Al composites reinforced with garnet⁹, albite¹⁰, quartz¹¹ and glass TiC¹² exhibited higher corrosion resistance compared to their matrix alloys. AlN particles which are highly insulating is reported to increase the susceptibility to pitting attack attributable to microgalvanic coupling between the matrix and the reinforcement and hydrolysis of AlN particles¹³. In the case of TiC-Al 2024 composites the TiC reinforcement is reported to decrease the anodic current density as well as amount and size of the pit¹⁴. Recent studies on the corrosion resistance

of TiB_2 ¹⁵ particulate reinforced A356 alloy show a marked decrease with increase in TiB_2 content is reported by Sun et al. The corrosion resistance of Al-Mg and Al-Cu composites is found to be higher than that of composites reinforced with mica particles¹⁶. The conflicting results can possibly be explained by differences in fabrication methods and composition which yield dramatically different electrochemical behavior¹⁷.

The observed variation of corrosion resistance in Al MMCs is attributed to chemical or mechanical factors such as composition of the matrix alloy, nature of reinforcing particles, fabrication methods, chemical or mechanical factors such as alloying, segregation, interfacial reactions, oxidized layers, residual stress around reinforced particles in the matrix and galvanic coupling between matrix and reinforcement. The corrosion behaviour of reinforced Al composites investigated⁴⁻¹⁶ in acidic, neutral, alkaline and various salt media reveal that Al composites suffer greater localized pitting corrosion in chloride ion environment compared to other media¹⁴⁻¹⁶.

Thus since Al MMCs lose their mechanical properties due to corrosion and lead to failure during service, research on the corrosion behaviour is equally important as the studies on fabrication and mechanical behaviour of Al MMCs.

The present investigation involves the study of corrosion behaviour of unreinforced Al-6061 matrix and its TiO_2 particulate composites in different electrolytes like NaCl, NaNO_3 and Na_2SO_4 . TiO_2 having high hardness and modulus is a good reinforcement for aluminium matrix, as it is known to enhance the corrosion resistance of the matrix. The main objective of present work is to establish the role and effectiveness of TiO_2 in the corrosion behaviour of Al 6061 composites.

MATERIALS AND METHODS

Materials Selection

Matrix alloy

Aluminium alloy 6061 used in the present investigation has the composition: Si – 0.6%, Fe – 0.1%, Cu – 0.3%, Mn – 0.02%, Mg – 0.8%, Zn, Cr, Ti – 0.01% each and remaining Al.

Reinforcement

TiO_2 , A.R Grade was obtained from E-Merck and Sigma Aldrich used as reinforcement in the form of particulates.

Composite preparation

The liquid metallurgy route using vortex technique (Stir Casting) is employed to prepare the composites. The composites were prepared with 2, 4 and 6 percentage by weight of TiO_2 using Crucible furnace fitted with a mechanical stirrer. Addition of reinforcement particulates in to the molten Al-6061 (800°C) was carried out by creating a vortex in the melt using a mechanical stainless steel stirrer coated with alumina (to prevent migration of ferrous ions from the stirrer material to the alloy). The stirrer was rotated at a speed of 450 rpm in order to create the necessary vortex. The ceramic particles were pre-heated to 400°C and added in to the vortex of liquid melt at a rate of 20 g/min. The ceramic particulates were of size ~100nm. The composite melt was thoroughly stirred and subsequently degasifiers were added. Castings were produced in permanent moulds in the form of cylindrical rods.

Specimen preparation

Cast material was cut into 20 x 20 mm cylindrical pieces using an abrasive cutting wheel. The matrix alloy was also cast under identical conditions as the composites, for comparison. The samples were successively ground using 240, 320, 400, 600, 800, 1000, 1500 and 2000 grade emery papers and were polished according to standard metallographic techniques and degreased in acetone and dried. For polarisation studies, the samples were cut as cylindrical rods (Diameter 1.128 cm) welded with brass rod (Diameter 4mm) for electrical connection and insulated on the outside using acrylic rubber mould to offer an active flat disc shaped bottom surface of 1cm². These working electrodes were also polished using 240, 320, 400, 600, 800, 1000, 1500 and 2000 grade emery papers and were polished according to standard metallographic techniques and degreased in acetone and dried.

RESULTS AND DISCUSSION

Open Circuit Potential Measurements

The evolution of the open circuit potential (OCP) was recorded for Al 6061 matrix alloy and its

TiO₂ composites (2, 4 and 6 wt %) in neutral 0.5N NaCl medium and the plots are shown in Fig.1. The plots and OCP values from the Table 1 reveal that increase towards the positive side as the percentage of TiO₂ reinforcement is increased in the composites. The increase in OCP values is in the noble direction from -0.8368 V for Al 6061 matrix alloy to -0.7841 V for reinforced composite (6 wt % TiO₂).

The shifting of OCP values to more positive side indicates that the TiO₂ particulates in the composites decrease the susceptibility of the composites towards corrosion. The TiO₂ reinforcement particles are perceived to act as physical barrier to the corrosion reaction on the Al 6061 matrix and thus impart good corrosion resistance to the Al 6061-TiO₂ composites.

TiO₂ being an insulator material, reduces the possible formation of microgalvanic regions in the composites compared to the matrix alloy, which accounts for the shift of OCP values to the positive side in the composites. The more noble behaviour of the composites with an increase in the TiO₂ content can also be related to the buildup of aluminium oxide at the surface^{18, 19, 20}.

Tafel Polarisation Measurements

Typical polarisation curves for Al 6061 matrix alloy and the composites containing 2, 4 and 6 weight % of TiO₂ particulates in 0.5N NaCl medium is shown in Fig.2. It is observed from the Tafel plots and Table 2 that both the corrosion current (I_{CORR}) values and the corrosion rates decrease with increase in TiO₂ content in the composites. This observation is similar to the findings in SiC reinforced Al composites⁴ by Bhat et al. that the composites exhibit reduced corrosion rate compared to the matrix alloy. The decrease in corrosion current with increase in TiO₂ content in the Al 6061 composites can be attributed to the reduced anodic areas for dissolution with increasing TiO₂ areas. The increased corrosion resistance in composites is believed to be due to the action of TiO₂ as physical barrier to the initiation and development of pitting corrosion, thereby modifying the microstructure of matrix.

Other reason for this variation could be the surface modifications like formation of protective layer of mixed oxo, hydroxo and chloro complexes at the interface. The increase in corrosion resistance of composites can also be perceived as due to an increased possibility of formation of magnesium intermetallic precipitates like Mg₂Si ($E_{\text{CORR}} = -1.536 \text{ V}$),

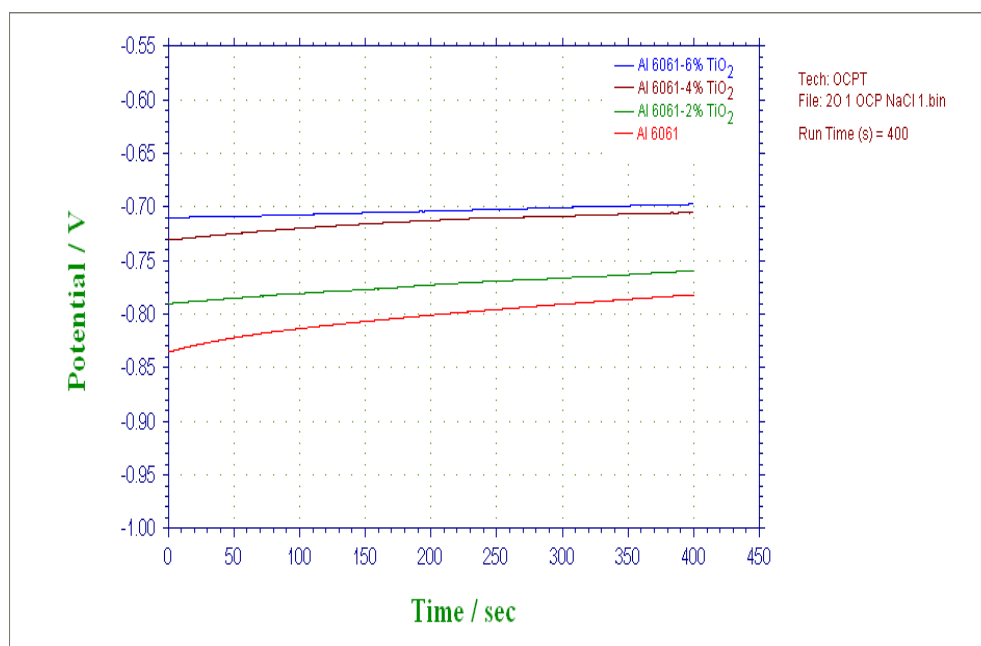


Fig. 1: Open circuit potentials for Al 6061 matrix alloy and its TiO₂ (2, 4 and 6 wt %) composites in 0.5N NaCl medium

Mg_2Al_3 ($E_{\text{CORR}} = -1.162 \text{ V}$), Mg_5Al_8 ($E_{\text{CORR}} = -1.050 \text{ V}$) at the particulate-matrix interfaces during fabrication. These magnesium intermetallic precipitates acting as sacrificial anodes protect the rest of the matrix, thereby restricting pit formation and its propagation^{21, 22, 23}. Wu Jianxin et al²⁴ have reported that the corrosion of particle reinforced Al based MMCs is not affected greatly by the presence of SiC particles and attributed the results to probable difference in the conducting nature of reinforcement. They have

proposed that the particles of reinforcement do play a secondary role as a physical barrier to initiation and development of pits and also modification in the microstructure of the material leading to reduced rate of corrosion.

Rodriguez²⁵ has shown that the improved mechanical properties of the particulate reinforced composites are reflected in the improved corrosion resistance of the materials. Extending along the

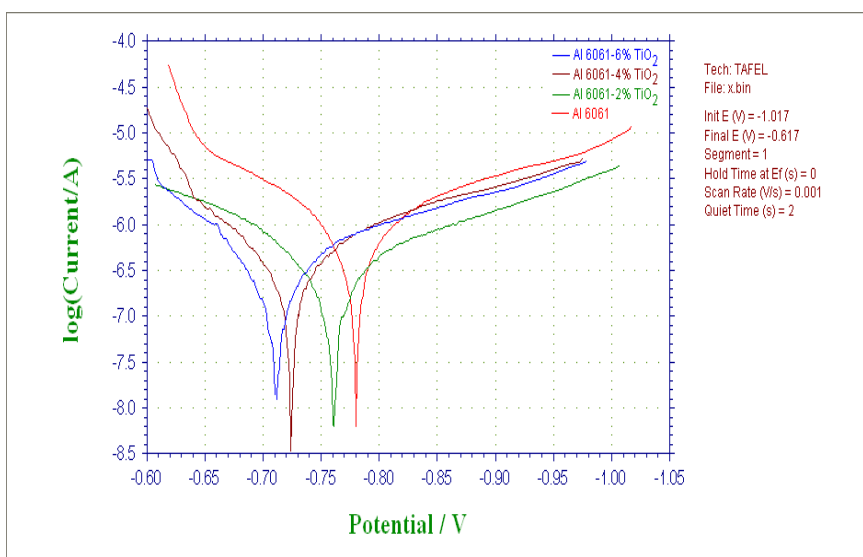


Fig. 2: Tafel polarisation and Cyclic polarisation plots for Al 6061 matrix alloy and its TiO_2 (2, 4 and 6 wt %) composites in 0.5N NaCl medium

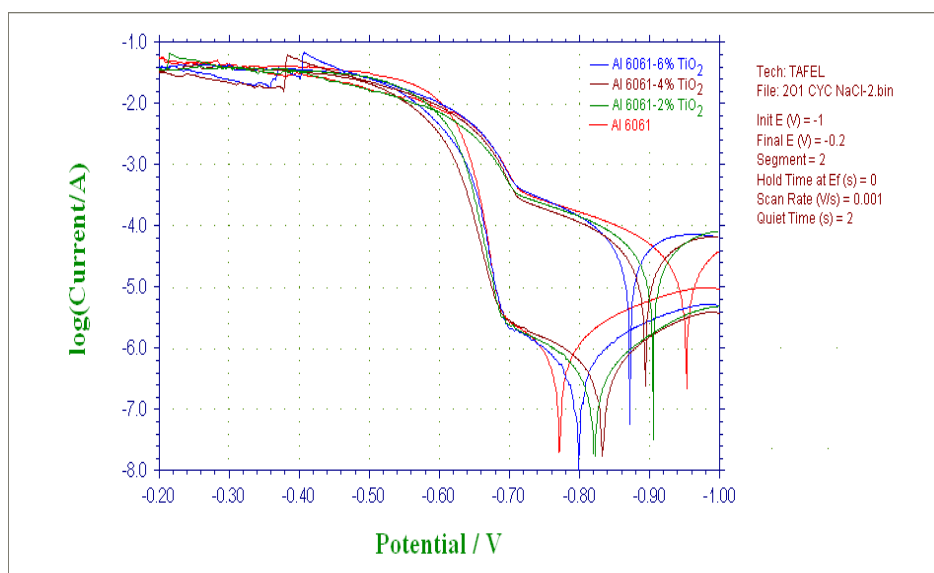
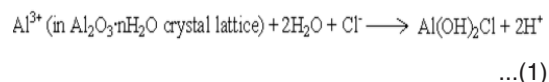


Fig. 3: SEM micrographs of Al 6061 matrix alloy and TiO_2 particles

same lines, the increased corrosion resistance of Al 6061-TiO₂ composites in our work, point towards improved mechanical properties of these composites. This is supported by the work of Ramesh et al²⁶ where increased content of TiO₂ in Al 6061 matrix is reported to result in higher hardness and lower wear coefficients. These results evidently point to the fact that TiO₂ reinforced composites has higher corrosion resistance as compared to the Al 6061 matrix alloy.

Earlier research workers have reported that halide ions play a significant role in pitting corrosion^{27, 28, 29}. Aluminum has good corrosion resistance since its passive film has very low solubility. However, pitting corrosion and other types of localized corrosion in case of aluminum occurs in neutral solutions as a result of the dominant influence of halogen ions, especially Cl⁻ ions. When Cl⁻ ion concentration increases, corrosion potential of aluminium becomes more negative, and aluminum tends to be more sensitive to pitting corrosion. It is believed that competitive adsorption promotes Cl⁻ ions instead of O or oxide on the aluminum surface so that pitting corrosion gets induced. However, the competitive adsorption theory cannot explain satisfactorily the dissolving mechanism of oxide film. According to complexation corrosion theory, compact Al₂O₃ film is expected to form on the aluminum surface in

neutral chloride medium offering good corrosion resistance³⁰. The Cl⁻ ions are adsorbed selectively on the crystal lattice of the oxide hydrate film under the effect of electric field. The complexation reaction of Cl⁻ with Al³⁺ hydrate ions occurs as given in Eqs. (1),



The above reaction results in activation of the aluminum crystallite boundary, so that crystallites break off from the film and become very resolvable and the thickness of the film decreases until local defects are formed. Cl⁻ ions erode the bare surface of Al matrix alloy easily. Once pitting corrosion occurs, the anode current density of small pits (or pit groups) would be much higher than that of a passive surface. Higher the Cl⁻ ion concentration, easier the complexation reaction occurs. That is to say that the dissolving velocity of pit becomes more rapid and therefore the critical pitting potential tends to be more negative with the increase of Cl⁻ ion concentration.

The passive film of the aluminum surface is destroyed by the Cl⁻ enrichment sites, which are the centres of pitting corrosion, and then pitting corrosion occurs when the electrode potential reaches the pitting potential. However, the exact mechanism

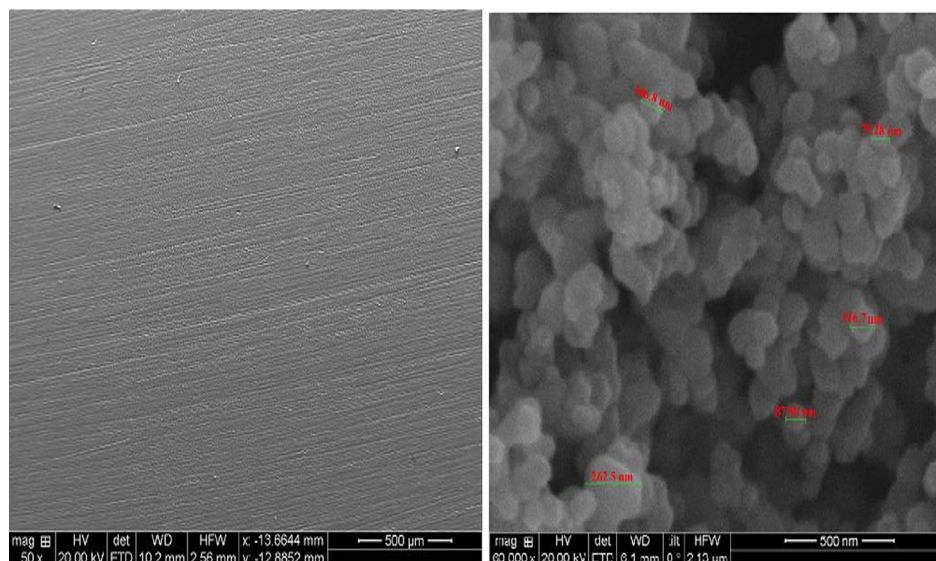


Fig. 4: SEM images of Al 6061 matrix alloy and its TiO₂ (2, 4 and 6 wt %) Composites taken after polarization studies in 0.5N NaCl medium

of breakdown of the passive layer by halide ions has not been very clearly understood, especially in the case of aluminium. The aluminium - air or aluminium - water interfaces consist of different solid aluminium oxy hydroxo complexes $Al[O_x(OH)_y(H_2O)_z]$ formed^{31, 32}. There is also some evidence for the transformation of the air formed passive layer of amorphous gelatinous alumina in moist air to pseudo-boehmite $(AlOOH)_4 \cdot H_2O$, boehmite $(AlOOH)$ and thereafter to bayerite $(Al(OH)_3)$ ^{33, 34}. The discrete structure of the passive layers of different composition can influence the corrosion resistance of Al against chloride induced pitting corrosion due to their different susceptibility to chloride attack.

The electrochemical study by Tomcsanyi³⁵ on Al and its alloys shows that the surface concentration of bonded chloride ions (as $AlOCl$ and $Al(OH)_2Cl$) is larger by two orders of magnitude than that of sulphate ions; chloride ions being bonded chemically in the interface. The highest corrosion rate observed in chloride medium is because chloride ions are more aggressive in pitting³⁶ due to their adsorbability on passive layer of aluminium compared to SO_4^{2-} and NO_3^- ions. The adsorption of chloride ions leads to the breakdown of protective oxide film³⁷.

Polarisation curves for the Al 6061 matrix alloy and its composites in 0.5N $NaNO_3$ and 0.5N

Table 1: Open circuit potentials of Al 6061 matrix alloy and its TiO_2 Composites in 0.5N NaCl medium

TiO_2 content in composites	OCP (E_{CORR}) values (in Volts)
0%	-0.8368
2%	-0.8198
4%	-0.7948
6%	-0.7841

Table 2: Corrosion current densities (I_{CORR}) and corrosion rates of Al 6061 matrix alloy and its TiO_2 composites in 0.5N NaCl medium

TiO_2 content in composites	Corrosion current density, I_{CORR} (Acm^{-2})	Corrosion Rate (mils per year)
0%	1.163×10^{-6}	0.4990
2%	4.958×10^{-7}	0.2414
4%	3.019×10^{-7}	0.1295
6%	1.368×10^{-7}	0.0586

Table 3: Pitting potentials (E_{PIT}), Repassivation Potentials (E_{RP}), ΔE_1 , E_{CORR} and ΔE_2 Values of Al 6061 matrix alloy and its TiO_2 composites in 0.5N NaCl medium

TiO_2 content in composites	E_{PIT} (V)	E_{RP} (V)	$\Delta E_1 = E_{PIT} - E_{RP}$ (V)	E_{CORR} (V)	$\Delta E_2 = E_{PIT} - E_{CORR}$ (V)
0%	-0.7002	-0.9505	0.2503	-0.7735	0.0733
2%	-0.6981	-0.9056	0.2075	-0.8020	0.1039
4%	-0.6959	-0.8953	0.1994	-0.8254	0.1295
6%	-0.6938	-0.8718	0.1780	-0.8397	0.1459

Table 4: Electrochemical parameters for Al 6061 matrix alloy and its TiO_2 (2, 4 and 6 wt %) composites in 0.5 N NaCl medium

TiO_2 content in composites	R_s (ohm)	R_p (ohm)	CPE(F)	Corrosion rate (mpy)
0%	2.420	9800	2.12×10^{-5}	0.4990
2%	2.829	12200	1.49×10^{-5}	0.2414
4%	3.769	22692	7.70×10^{-6}	0.1295
6%	4.008	26496	5.97×10^{-6}	0.0586

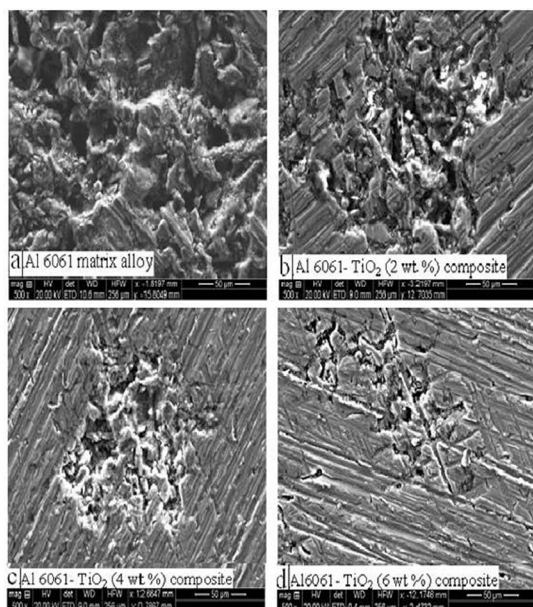


Fig. 5: EDX spectra of Al-Fe-Si rich phase and TiO₂ phase in Al 6061-TiO₂ (6 wt %) composite

Na₂SO₄ are identical and exhibit the same trend as observed in 0.5N NaCl medium. Physical examination of the samples reveals significant pitting in chloride medium while pitting is insignificant in both nitrate and sulphate media. It is observed that the corrosion rate is lower in both nitrate and sulphate media, for matrix as well as composites; this can be attributed to their ability to suppress both cathodic and anodic currents³⁸. A comparison of the results in all the media indicates that the relative degree of corrosion in different ionic species follows the order Cl⁻ > NO₃⁻ > SO₄²⁻. The lowest corrosion rate observed in SO₄²⁻ medium is probably due to the formation of passive aluminium sulphate which is less soluble than other salts formed in the presence of Cl⁻ and NO₃⁻ ions.

Cyclic Polarisation Measurements

Cyclic polarisation curves for Al 6061 matrix alloy and the composites containing 2, 4 and 6 weight % of TiO₂ particulates in 0.5N NaCl

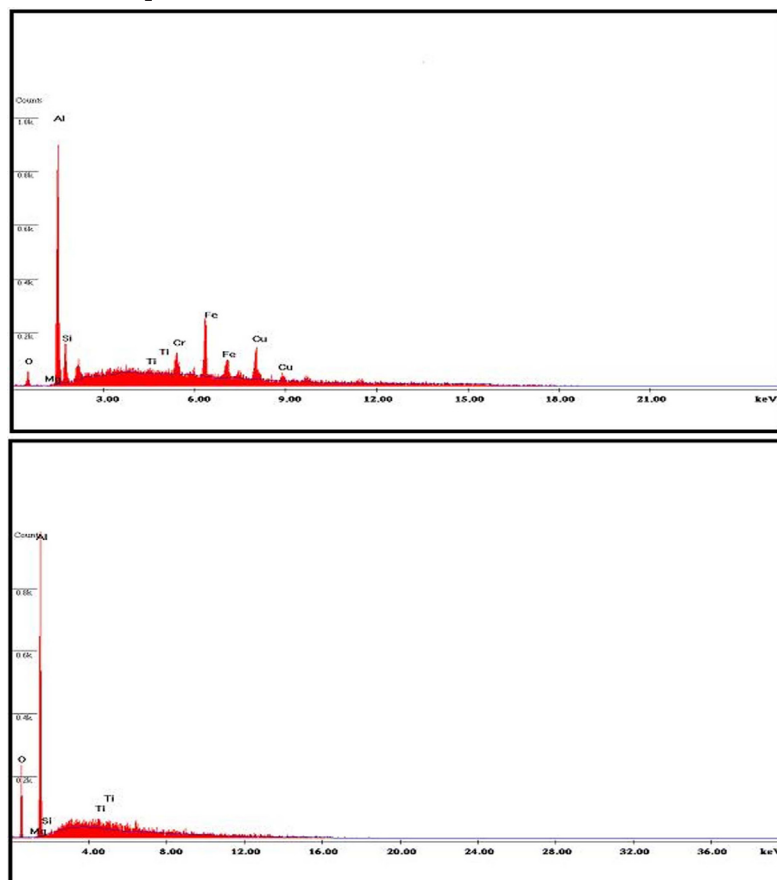


Fig. 6: EDX spectrum of Mg₂Si phase in Al 6061-TiO₂ (6 wt %) composite

solution are shown in Fig.2. More negative values of the repassivation potentials compared to the pitting potential indicates possible occurrence of pitting. The size of the pitting loop is a rough indication of pitting susceptibility, the larger the loop, the greater the tendency to pit.

From the Fig.2 and Table 3, (Pitting potentials (E_{PIT}), Repassivation potentials (E_{RP}) and ΔE_1 ($E_{PIT} - E_{RP}$) values, it is evident that the pitting potentials of the TiO_2 reinforced composites are more positive than those of the matrix alloy. The pitting potential increases in the noble direction with increase in TiO_2 contents and ΔE_1 values decreases from the matrix alloy to composites. This indicates that the composites are less active and less prone to pitting compared to the matrix alloy. ΔE_1 is the direct measure of pitting susceptibility and is used to assess the repassivation behaviour of propagating pits, the ease with which local active sites can be eliminated³⁹. The matrix alloy exhibits larger pitting loop as indicated by higher ΔE_1 value. In the composites, ΔE_1 values decrease with increase in TiO_2 content, showing inhibitive action of the TiO_2 particulates.

This behavior of the composites in comparison with the matrix confirms the results of our studies viz., OCP and Tafel polarization. Pitting corrosion occurs mainly on the heterogeneities of

the metals and alloys in the passive state due to disruption of the passive layer by aggressive species like Cl^- and ClO_4^- ions in the environment^{41, 42}.

The other factors influencing corrosion in the composites include porosity of the material, segregation of alloying elements at the matrix-reinforcement interface, presence of interfacial reaction product, high dislocation density around the reinforcement phase and voids at the interface^{14, 43}. The presence of a less conductive TiO_2 phase does not provide any path for electron exchange during oxygen reduction and drives the anodic reaction at a lower rate in the composites as compared to matrix alloy.

ΔE_2 value is a measure of the width of the passive region in the polarization curves and provides information about the resistance of materials to corrosion. Higher the ΔE_2 value, greater is the corrosion resistance of composites⁴⁴. The ΔE_2 value of 73.3 mV for Al 6061 matrix alloy is found to increase to 145.9 mV for Al-6 wt% TiO_2 composite. This clearly shows that the addition of noble insulator TiO_2 to Al 6061 matrix significantly increases the passive range from the unreinforced matrix alloy to the reinforced composites. The presence of insulating TiO_2 particles can influence the corrosion behaviour of Al 6061- TiO_2 composites in two ways.

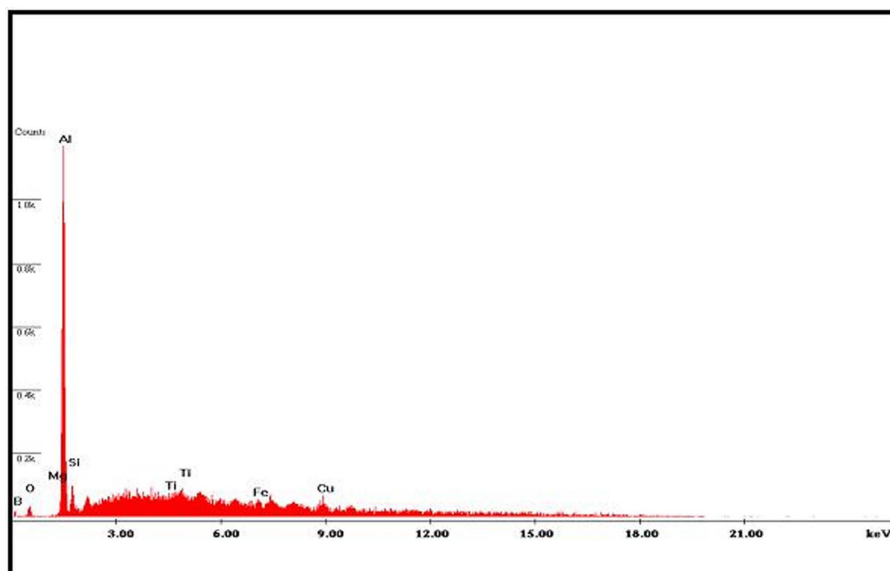


Fig. 7: XRD pattern of Al 6061 matrix alloy and TiO_2 particles

It is generally agreed that insulating particulates like TiO_2 can influence corrosion, modifying the microstructure of the MMC by altering the size and distribution of intermetallic phases or introducing residual stresses between reinforcement and matrix. The presence of TiO_2 particles does influence passive current density and pitting potential of aluminium, to an extent such that the pitting resistance of passive film on aluminium gets significantly affected³⁸. Generally the susceptibility to pit initiation is similar for composites and unreinforced alloys; however, the rate of pit

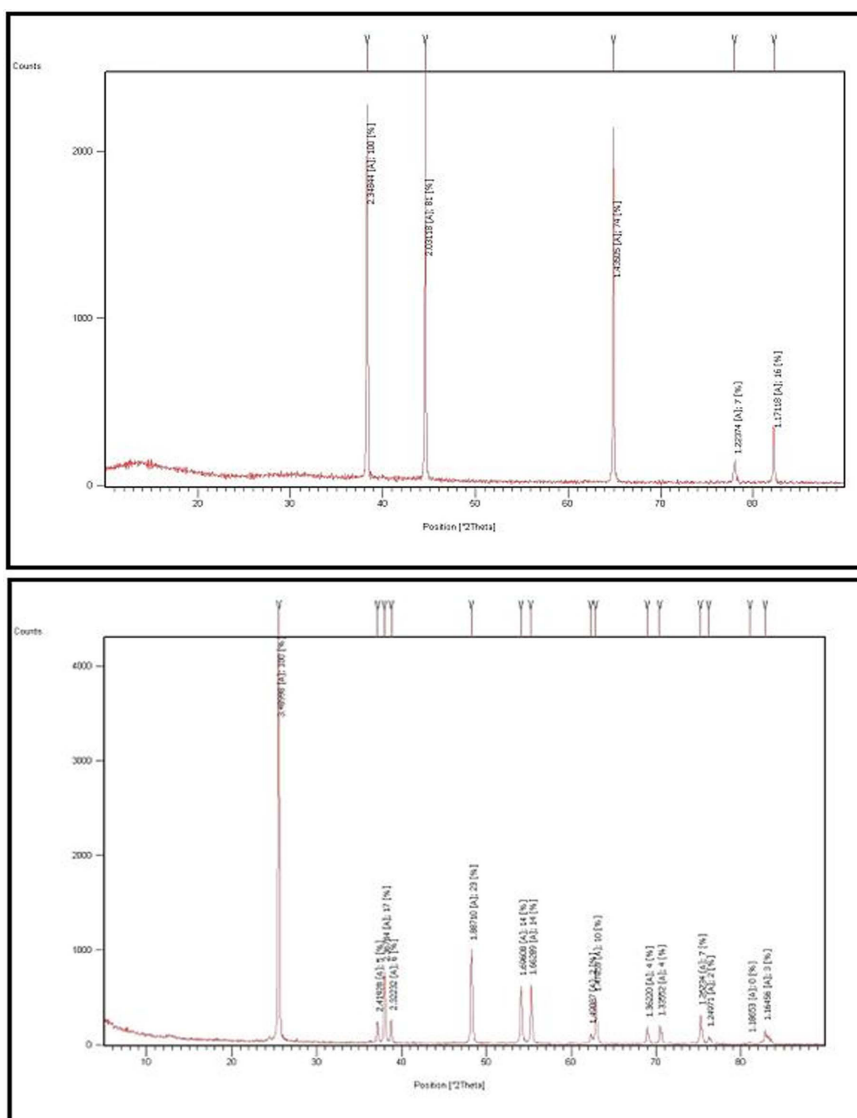


Fig. 8: XRD pattern of Al6061- TiO₂ (6 wt %) composite

propagation is observed⁴⁸ to be slightly lower for composites contrary to the work of Aylor et al.

Scanning Electron Microscopy

Scanning electron microscopy images of Al 6061 matrix alloy before corrosion test and that of reinforcement TiO_2 particles are shown in Fig.3.

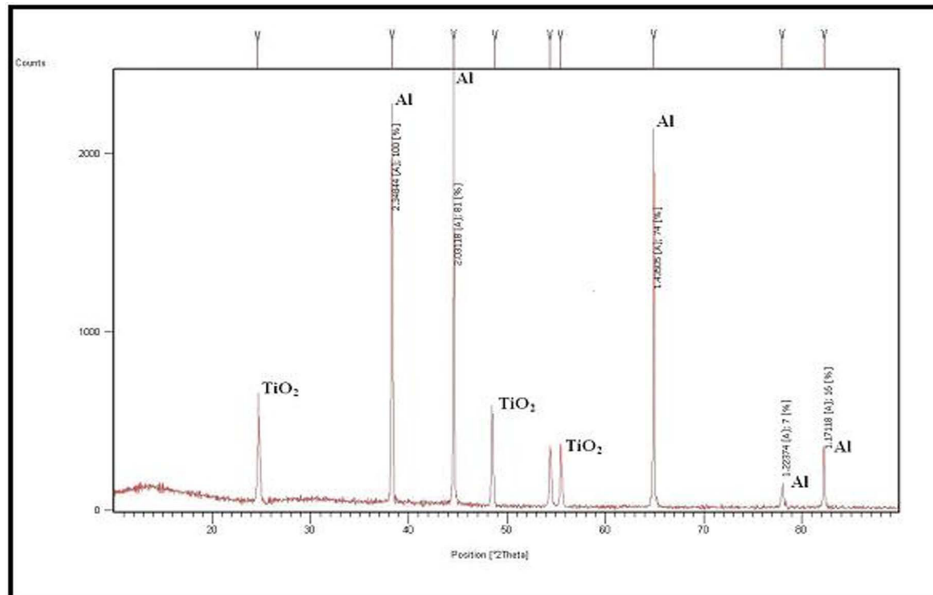


Fig. 9: Nyquist plots of the Al 6061 matrix alloy and its TiO_2 (2, 4 and 6 wt %) composites in 0.5 N NaCl medium

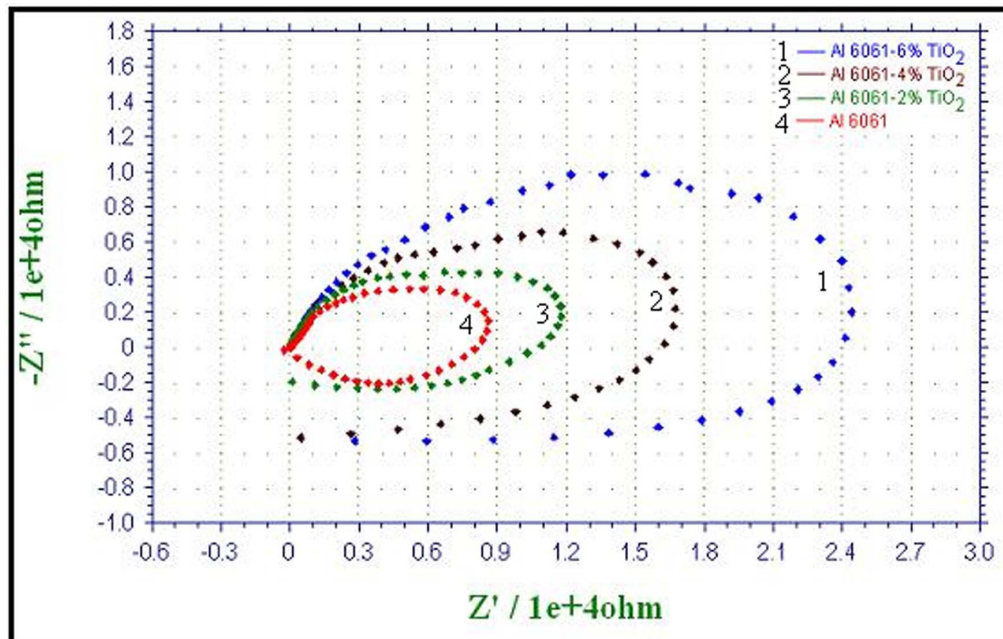
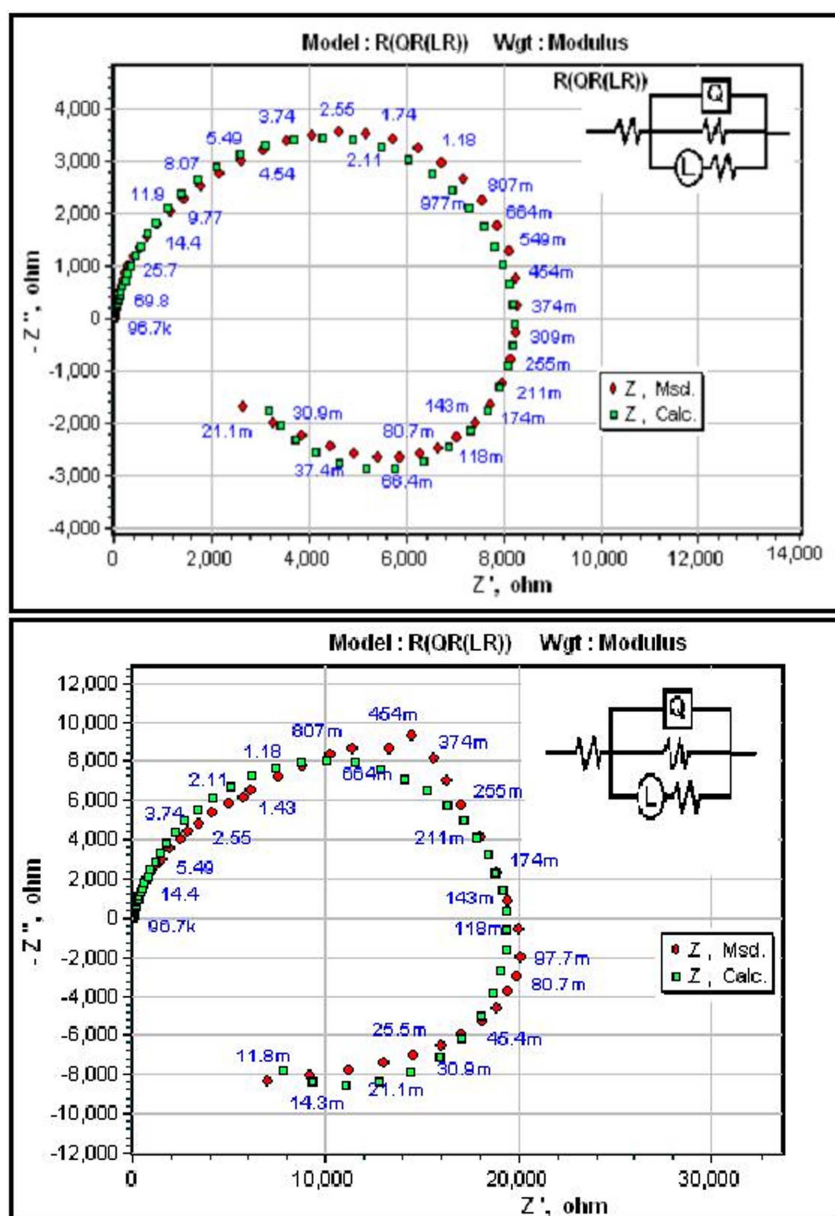


Fig.10: Equivalent circuit model used to fit the experimental data of Al 6061 matrix alloy and Al 6061- TiO_2 (6 wt %) composite in 0.5N NaCl medium



composites indicates the higher corrosion resistance of composites than matrix alloy

The micrographs of matrix alloy and the composites reveal a complete deterioration of smoothness of surface suggesting the penetration of chloride ions in to the material surface forming corrosion spot. A comparison of SEM micrographs of the samples after polarization studies also suggests morphological modifications probably due to the reaction of Mg_2Si phase. Corrosion products resulting from the reaction of Mg_2Si prevent further dissolution of the particle and reduce the effect of galvanic coupling with the matrix, thus improving corrosion resistance of composites⁵¹. In general, Mg_2Si phase acts as anode with respect to matrix alloy and forms a galvanic couple leading to pitting corrosion. But Mg_2Si is also likely to form oxides like MgO and SiO_2 , which offer protection to the Mg_2Si particles and thereby decrease the number of regions of galvanic coupling between Mg_2Si and matrix⁵².

Energy Dispersive X-ray Analysis

The EDX spectrum shows the presence of various elements in the TiO_2 reinforced Al 6061 surface. The EDX analysis of the two regions (i) the intermetallic phases and (ii) the TiO_2 rich phase in the EDX spectrum are presented in Fig.5 and Fig.6. It is observed that the matrix alloy and composites contain the Al-Fe-Si rich and Mg_2Si intermetallic phases.

The presence of more intense peaks for Al, Mg, Fe and Si as shown in Fig.5 strongly indicates the existence of Al-Fe-Si rich intermetallic phases like Fe_2SiAl_8 and Mg_2Si . These intermetallic phases being conductive act anodically with respect to Al 6061 matrix alloy and become the preferable sites for initial localised attack thus causing pits⁵³. The surface morphological studies around the pits reveal that the corrosion is concentrated around the intermetallics but not around the insulator TiO_2 particles which is confirmed by EDX analysis of pits. The presence of Fe and Si suppresses the cathodic reaction rate of the aluminium based intermetallics rich in Fe.

XRD Studies

The XRD patterns of Al 6061 matrix alloy, TiO_2 particulates and that of composite (6 wt% TiO_2

reinforced) are given in Fig.7 and Fig.8 respectively. The XRD spectra of the composite clearly exhibits the major 2 θ peaks of Al 6061 matrix (at 38.29°, 44.57° and 64.92°) and TiO_2 (25.52°, 48.22° and 54.07°) indicating the incorporation of the reinforcement particulates in the matrix alloy.

EIS Studies

The EIS plots and data which follow reveal that the impedance curve consists of a large capacitive loop at high frequencies (HF) and a small inductive one at low frequencies. Nyquist plots of the Al matrix alloy and its TiO_2 composites in 0.5 N NaCl solution is given in Fig.9. The HF capacitive loop is attributed to the presence of a protective oxide film at the surfaces of composites^{54, 55}. The HF loop could be assigned to the relaxation process in the hydrated aluminium oxide film and its dielectric properties. The oxide film is considered to be a parallel circuit of a resistor corresponding to the ionic conduction in the oxide film and a capacitor due to its dielectric properties.

The inductive loop observed at low frequencies may be attributed to the relaxation process in adsorbed species OH^-_{ads} present on the surface of the samples. The numerical values of the polarisation resistance R_p and the double layer capacitance C_{dl} were determined by analysis of the complex plane impedance plots and the equivalent circuit model by using a computer program. The charge transfer controlled type corrosion process has been confirmed by the presence of semicircles in the impedance diagrams^{56, 57}. Based on the analysis of the impedance spectra, an equivalent circuit model $R[QR[LR]]$ is being proposed for both the matrix alloy and composites (Fig.10), after simulating their electrochemical behaviour. The equivalent circuit consists of a constant phase element (CPE) Q in parallel with the parallel resistors R_i (charge transfer resistance) and R_L (inductance resistance) and the latter is in series with the inductor L . In this case the polarisation resistance can be calculated using the Eqs. 2),

$$R_p = \frac{R_L \times R_i}{R_L + R_i} \quad \dots(2)$$

The electrochemical parameters of Al 6061 matrix alloy and its composites obtained from EIS

studies are given in Table 4. The measured value of polarization resistance, R_p increases while the constant phase element, CPE value decreases with increase in TiO_2 content. Hence our results show that the corrosion rate decreases with increase in the content of TiO_2 reinforcement.

It can be observed from the Nyquist plots, that the radius of the capacitive loops above the real axis increases with increase in TiO_2 content for composites. Our results indicate that the polarisation resistance R_p value increases with increase in TiO_2 content in composites confirming improved corrosion resistance in composites. These results complement potentiodynamic polarisation studies.

CONCLUSIONS

The corrosion behaviour of unreinforced Al 6061 matrix alloy and its composites reinforced with TiO_2 (2, 4 and 6 wt %) were studied in 0.5N NaCl medium. The observations of these studies lead to the following conclusions,

1. With increase in the reinforcement content in the composites, the OCP values increase in the noble direction indicating higher corrosion resistance imparted by the TiO_2 particulates.
2. In each case, it was observed that the corrosion potential E_{CORR} values shift towards negative direction with increase in the concentration of the chloride medium, probably due to the breakdown of stable oxide film on Al matrix as a result of increased adsorption of chloride ions on the Al surface or its oxide layer.
3. Corrosion rates of the matrix alloy and the composites were calculated from the Tafel polarization curves, which show a decrease with increase in the content of the reinforcement. The increased corrosion resistance in composites is believed to be due to reinforcement particulates modifying the microstructure of matrix and also acting as physical barrier to the initiation and development of pitting corrosion.
4. Pitting potentials E_{PIT} are found to increase

in the anodic direction from the matrix alloy to reinforced composites while the pitting loop size ($\Delta E_1 = E_{\text{PIT}} - E_{\text{PP}}$) decreases with increasing content of reinforcement, confirming the increased corrosion resistance due to reinforcement in Al 6061 matrix alloy.

5. A comparison of the results from all the media indicates that the relative degree of corrosion in different ionic species follows the order $\text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. The lowest corrosion rate observed in SO_4^{2-} medium is due to the formation of passive aluminium sulphates which are less soluble than those salts formed in presence of Cl^- and NO_3^- ions.
6. The XRD and EDX analysis of all the composites confirm the positive inclusion of the reinforcement particulates in the matrix alloy and also the presence of intermetallic phases like Mg_2Si , Al_3Fe and Al_4C_3 formed at matrix-reinforcement interface.
7. SEM pictures of each of the composites and the unreinforced alloy clearly reveal severe deterioration of the surface of both matrix alloy and its composites of all the reinforcements. However there is a decrease in the extent of pit formation in the composites as compared to the matrix alloy corroborating the results of the corrosion studies.
8. The Nyquist plots of the matrix alloy and the composites in NaCl medium show semicircles indicating that the corrosion process is mainly charge transfer controlled. The measured value of polarization resistance R_p increases while the CPE value decreases with increase in content of the reinforcement in all the cases.

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REFERENCES

1. J E Allison and G S Cole., *J. Met.* **45**: 19-24 (1993).
2. C G E Mangin, J A Isaacs, J P Clark, *J. Met.* **48**: 49-51 (1996).
3. H G Kang, D L Zhang, B Cantor, *J. Microstrc.* **169**: 239-245 (1993).
4. M S N Bhat, M K Surappa, Sudhaker Nayak, *J. Mat. Sci.* **26**: 4991-4996 (1991).
5. S L Pohlman, *Corrosion.* **34**: 156-159 (1978).
6. P P Trzaskoma, E McCafferty, C R Crowe, *J. Electrochem. Soc.* **130**: 1804-1809 (1983).
7. Rahul Mitra, Yashwanth R. Mahajan, *Defense Sci. J.* **43**: 397-418 (1993).
8. J B Fogangolo, M H Robert, Ruiz-Navas, J M Torralba, *J. Mat. Sci.* **39**: 127-132 (2004).
9. K H W Seah, M Krishna, V T Vijayalashmi, J Uchil, *Corros. Sc.* **44**: 917-925 (2002).
10. S C Sharma, *Corros. Sci.* **43**: 1877-1889 (2001).
11. K H W Seah, B.M.Sathish, *Mater. Design.* **17**: 245-250 (1996).
12. H C Ananda Murthy , Somit Kumar Singh, *Adv. Mater. Lett.* **6**(7): 633-640 (2015).
13. Zhang Sheng Liu, Wu, Bian Tao, Gu Ming Yuan, *J. Mat. Sci.* **42**(14): 5736-5741 (2007).
14. A. Albiter, A. Contreras, M. Salazar, G. J. Gonzalez, Rodriguez, *J. Appl. Electrochem.*, **36**: 303-308 (2006).
15. H.H.Sun, D.Chen, X.F.Li, N.H.Ma, H.W.Wang, *Mater. Corros.*, **60**: 419-423 (2009).
16. D.Nath, T.K.G.Namboodhiri, *Corros. Sci.* **29**: 1215-1229 (1985).
17. D.G.Kolman, D.P.Butt, *J. Electrochem. Soc.* **144**: 3785-3791 (1997).
18. A.M.Shams El Din, N.J.Paul, *Thin solid films.* **189**: 205-216 (1990).
19. J.M.Abd El Kader, A.M. Shams El Din, *Br. Corros. J.* **14**: 40-45 (1979) .
20. A.M.Shams El Din, A.A. Hammound, *Thin solid films.* **167**: 269-280 (1988).
21. N.N.Birbilis, R.G.Buchheit, *J. Electrochem. Soc.* **152** (4): 140-151 (2005) .
22. R.G. Buchheit, *J. Electrochem. Soc.* **142**: 3994-3996 (1995).
23. KHW Seah, M Krishna, V T Vijayalakshmi, J Uchil, *Corrosion.* **44**: 761-772 (2002).
24. W.Jiaxian, W.Liu, P.X.Li, R.Wu, *J. Mat. Sci. Lett.* **12**: 1500-1501 (1993).
25. E.L.Rodreguez, *J. Mat. Sci. Lett.* **6**: 718-720 (1987) .
26. C.S.Ramesh, A.R.Anwar Khan, N. Ravi Kumar, P. Savanprabhu, *Wear.* **259**: 602-608 (2005).
27. T.P.Hoar, W.R.Jacob, *Nature.* **216**: 1299-1301 (1967).
28. T.E.Pou, O.J, Murphy, V.Young, O.M.Bokris. *J. Electrochem. Soc.* **131**: 1243-1251 (1984) .
29. N.Sato, *Corros. Sci.* **27**: 421-433 (1987).
30. Cheng-Hao Liang Wei Zhang, *J. Chin. Chem. Soc.* **53**: 313-318 (2006).
31. A.Berzins, R.T.Lowson, K.J.Mirans, *Aust. J. Chem.* **30**: 1891 (1977).
32. W.C.Moshier, G.D.Davis, J.S.Ahearn, *Corros. Sci.* **27**: 785-801 (1987).
33. K.Wefers, G.M.Bell, Alcoa Technical paper No. **19**: 1-47 (1972).
34. T.Okada, *Corros. Sci.* **26**: 839-849 (1986).
35. Tomcsanyi L, Varga K, Bartik I, Horanyi G, Maleczki E, *Electrochim. Acta* **34**: 855-859 (1989) .
36. H.C. Ananda Murthy, V. Bheema Raju and C. Shivakumara, *Bull. Mater. Sci.* **36**:1057-1066 (2013).
37. M. A. Paez, O. Bustos, G. E. Thompson, P. Skeldon, K. Shimizu, G. C. Wood, *J. Electrochem. Soc.* **147**: 1015-1020 (2000).
38. P.C.R. Nunes, L.V.Ramanathan, *Corros. sci.* **51** (8): 610-617 (1995).
39. J.Bienias, M.Walczak, B.Surowska, J.Sobczak, *J. OptoeIn. and Adv. Mat.* **5**: 493-502 (2003).
40. J.Datta, B.Samantha, A.Jana, S.Sinha, C.Bhattacharya, S.Bandyopadhyay, *Corros. Sci.* **50**: 2658-2668 (2008) .
41. Mohammed A. Amin, Sayed S. Abd El Rehim, S.O.Moussa, Abdallah S.Ellithy, *Electrochim. Acta.* **53**: 5644-5652 (2008).
42. G.Wrangler, WNT Warszawa, (1985).
43. R.L.Deuis, L.Green, C.Subramaniyan, J.M.Yellup, *Corrosion* **53**: 880-890 (1997).
44. S.L.Winkler, M.P.Ryan, H.M.Flower, *Corros. Sci.* **46**: 893-902 (2004).
45. A.Mortensen, M.N.Gungor, J.A.Cornie, M.C.Flemings, *J. Met.* **32**: 30-35 (1986).

46. A.Mortensen, V.Michuad, *Metall. Trans. A* **21**: 2069-2072 (1990).
47. A.Mortensen, J.A.Cornie, M.C.Flemings, *Metall. Trans. A* **19**: 709-712 (1988).
48. D.M.Aylor, D.Taylor, Corrosion of Metal Matrix Composites in ASM Handbook, Vol. **13**, Corrosion, J.R Davis Ed., ASM International, Materials park, OH (1999) 859-863.
49. K.Mahadevan, K.Raghukandan, B.C.Pai, U.T.S.Pillai, *Ind. J. Engg. and Mat. Sci.* **14**: 277-281 (2007).
50. W.A. Badawy, F.M, Al-Kharafi, A.S. El-Azab, *Corros. Sci.* **41**: 709-727 (1999).
51. R.Escalera-Lozano, M.A. Pech-Canul, M.I. Pech-Canul and P.Quintana, *Mater. Corros.* **60**: 683-689 (2009).
52. R.Escalera-Lozano, M.I. Pech-Canul, M.A. Pech-Canul, M.Montoya- Davila, A.Uribe-Salas, *The open corrosion journal*, **3**: 73-79 (2010).
53. L.H.Hihara, T.S.Devarajan, Hongbo Ding, G.A. Hawthorn, Tri-Service corrosion conference, (2005).
54. C.M.A.Brett, *Corros. Sci.* **33**: 203-210 (1992).
55. C.M.A.Brett, *J. Appl. Electrochem.* **20**: 1000-1003 (1990).
56. G.Trabanelli, C.Montecelli, V.Grassi, A.Frignani, *J. Cem. Concr. Res.* **35**: 1804-1813 (2005).
57. Irfan aziz, Qi Zhng, *Int. J. Phy.* **B 23**: 1497-1515 (2009).