



## Corrosion Characterization of TiO<sub>2</sub> Particulate Reinforced Al-6063 Composites in Chloride and Nitrate Media

V. BHEEMA RAJU<sup>1\*</sup>, H.C. ANANDA MURTHY<sup>2</sup> and P.F. SANALLA<sup>3</sup>

<sup>1</sup>Department of Chemistry, Dr. Ambedkar Institute of Technology, Mallathahalli, Bangalore-560 056, India

<sup>2</sup>Department of Chemistry, R.N. Shetty Institute of Technology, Channasandra, Bangalore-560 061, India

<sup>3</sup>Department of Chemistry, H.K.B.K. College of Engineering, Bangalore-560 045, India

\*Corresponding author: Fax: +91 80 23217789; Tel: +91 80 23211505; E-mail: vbrajuit@gmail.com

(Received: 29 June 2010;

Accepted: 11 December 2010)

AJC-9383

The corrosion behaviour of Al 6063-TiO<sub>2</sub> particulate composites in chloride and nitrate media has been studied in the present investigation. The unreinforced matrix and the composites containing 2, 4 and 6 % by weight of TiO<sub>2</sub> particulates were prepared by liquid metallurgy route using vortex technique. The potentiodynamic polarization experiments revealed that the composites are susceptible to corrosion compared with their matrix alloy. Moreover, the corrosion rates of the composites markedly increases with increase in the TiO<sub>2</sub> content. The pitting effect was more pronounced in presence of aggressive Cl<sup>-</sup> ions compared to mild NO<sub>3</sub><sup>-</sup> ions. The observed lower corrosion resistance in composites could be attributed to the microgalvanic coupling between the intermetallics around the reinforcement particles such as Mg<sub>2</sub>Si, AlTi<sub>3</sub> and matrix alloy. Insulator TiO<sub>2</sub> particulates are perceived to act as inert material and degrade the integrity of the protective oxide layer on the Al matrix alloy. SEM and EDX analysis of samples in chloride media showed the presence of large pits and completely deteriorated surface, complementing polarization studies.

**Key Words:** Al6063 composites, TiO<sub>2</sub> particulates, Microgalvanic coupling, Intermetallics, SEM, EDXA.

### INTRODUCTION

Metal matrix composites (MMCs) possess significantly improved properties including high specific strength; specific modulus, damping capacity and good wear resistance compared to unreinforced alloys. Particulate reinforced Al metal matrix composites (PMMCs) have significant applications in various sectors such as structural avionics, automobiles, transport, nuclear and electronics industries. They are used as good substitutes for aluminium in automotive pistons, brakes, brake-drums, clutch discs, electronic substrates, *etc.*, owing to their better physical and mechanical properties. Aluminium alloys reinforced with SiC, B, Al<sub>2</sub>O<sub>3</sub>, TiC, ZrB<sub>2</sub>, AlN, graphite, garnet, albite, fly ash, red mud and quartz particulates are known for their attractive characteristics such as high specific modulus, high specific strength, low thermal expansion coefficient, light weight and low cost<sup>1-3</sup>. Corrosion studies published on Al-PMMCs in various salt media revealed significant variation in the corrosion resistance of composites. Corrosion studies published on aluminium alloys reinforced with SiC<sup>4</sup>, B<sup>5</sup>, Al<sub>2</sub>O<sub>3</sub><sup>6</sup>, TiC<sup>7</sup> and ZrB<sub>2</sub><sup>8</sup> reveal that corrosion resistance of composites are lower than matrix alloys, owing to galvanic corrosion. However garnet<sup>9</sup>, albite<sup>10</sup>, quartz<sup>11</sup> and glass fibre<sup>12</sup> reinforced

Al composites exhibited higher corrosion resistance compared to their matrix alloys. The corrosion behaviour of reinforced Al composites has been earlier investigated<sup>4-18</sup> in acidic, neutral, alkaline and various salt media. Previous studies reveal that Al composites suffer localized pitting corrosion in chloride ion environment compared to other media<sup>13-15</sup>. The observed decrease in resistance to corrosion in Al-MMCs is attributed to chemical or mechanical factors such as alloying segregation, interfacial reactions, porosity, oxidized layers, residual stress around reinforced particles in the matrix<sup>16</sup> and galvanic coupling between matrix and reinforcement<sup>5</sup>. Al-6061 matrix has been an attractive matrix alloy for particulate reinforced composites which offer enormous prospects in space and avionic sectors<sup>17</sup>.

The present investigation involves the study of corrosion behaviour of unreinforced Al6063 matrix and TiO<sub>2</sub> particulate reinforced composites in different electrolytes like NaCl and NaNO<sub>3</sub>. The investigation was conducted using potentiodynamic polarization method. Scanning electron micrograph (SEM) and energy dispersive X-ray (EDX) examinations of the electrode surface were also performed. TiO<sub>2</sub> Particulate reinforced Al-6063 composites exhibit marked decrease in corrosion resistance when compared to matrix alloy.

## EXPERIMENTAL

**Aluminium alloy 6061-matrix:** Aluminium alloy 6061 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<sub>2</sub>, A.R. grade was obtained from E-Merck and used as reinforcement in the form of particulates.

**Composite preparation:** The liquid metallurgy route using vortex technique is employed to prepare the composites. The composites were prepared containing 2, 4 and 6 % by weight of TiO<sub>2</sub>. Addition of reinforcement material TiO<sub>2</sub>, in to the molten Al-6061 alloy melt 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 TiO<sub>2</sub> particles were pre-heated to 400 °C and added in to the vortex of liquid melt at a rate of 120 g/min. The TiO<sub>2</sub> particulates were of size *ca.* 100 nm. The composite melt was thoroughly stirred and subsequently degasifiers were added. Castings were produced in permanent moulds in the form of cylindrical rods (diameter 30 mm and length 150 mm).

**Specimen preparation:** Casted material was cut into 20 mm × 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 polarization studies, the electrodes were cut as cylindrical rods, welded with brass wire for electrical connection and moulded using acrylic rubber to offer an active flat disc shaped surface of 1 cm<sup>2</sup>. Working electrode is polished as described above.

### Corrosion test: Potentiodynamic polarization method:

Polarization measurements were carried out on Model 600 C series, Electrochemical Analyzer/Workstation, CH Instruments, USA. All experiments were carried out using a three electrode cell with saturated calomel electrode (SCE) and platinum electrode as reference and counter electrode respectively. The SCE was connected *via* Luggin capillary, the tip of which was very close to the surface of the working electrode to minimize the IR drop. Open circuit potential (OCP) measurements were recorded for 1 h, the time necessary to reach quasi stationary state for open circuit potential, followed by polarization measurements at a scan rate of 1 mV/s for Tafel plots.

**Energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) analysis:** Following the polarization studies, the corroded samples were subjected to energy dispersive X-ray analysis using model Oxford Link ISIS, UK, to gain more insight on the composition of the corrosion products formed at the tested Al matrix and composites. The morphology of the passive layer and the corrosion products formed on the electrode surface was examined by scanning electron micrograph (SEM) using model JSM-840A SEM, JEOL, Japan.

## RESULTS AND DISCUSSION

Typical polarization curves for Al6063 matrix alloy and the composites containing 2, 4 and 6 % by weight of TiO<sub>2</sub>

particulates, in decinormal solution of NaCl are shown in Fig. 1. Similar plots are obtained for the matrix and the composites in 0.1 N NaNO<sub>3</sub> medium as well (hence not reproduced here). The evaluated electrochemical corrosion parameters for the matrix alloy and the composites in 0.1 N and 0.5 N NaCl are given in Table-1. It can be observed from the Tafel plots and Table-1 that the corrosion current ( $I_{\text{corr}}$ ) values and the corrosion rate increase with increase in TiO<sub>2</sub> content in the composites. These results point to the fact that TiO<sub>2</sub> reinforced composites have lower corrosion resistance as compared to matrix alloy in chloride medium as well. This observation is similar to the findings of Bhat *et al.*<sup>4</sup> in Al-SiC composites, that composites exhibit reduced corrosion resistance compared to the matrix alloy. The small shift of corrosion potential values to the negative side in composites is indicative of defect oxide layer formation in the presence of reinforcement in the matrix alloy<sup>19</sup>.

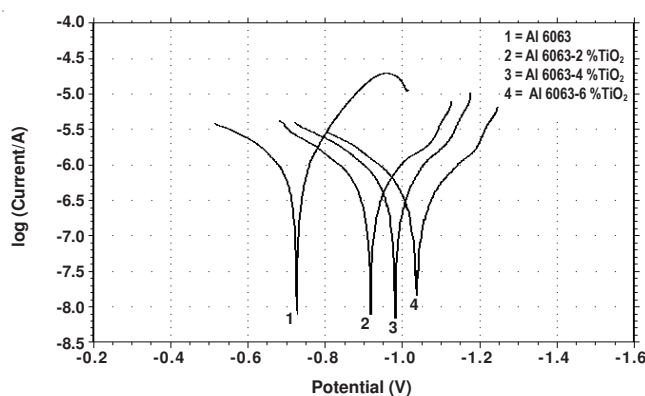


Fig. 1. Tafel plots of Al6063 matrix (0 %) and its TiO<sub>2</sub> composites (2, 4 and 6 %) in 0.1 N NaCl medium

TABLE-1  
ELECTROCHEMICAL CORROSION PARAMETERS OF  
Al6061 AND ITS TiO<sub>2</sub> COMPOSITES IN 0.1 N NaCl  
AND 0.5 N NaCl SOLUTIONS

Composite (% TiO <sub>2</sub> )	0.1 N NaCl		0.5 N NaCl	
	$I_{\text{corr}}$ (Acm <sup>-2</sup> )	Corrosion rate (mils per year)	$I_{\text{corr}}$ (Acm <sup>-2</sup> )	Corrosion rate (mils per year)
0	$3.388 \times 10^{-7}$	0.0726	$4.011 \times 10^{-7}$	0.086
2	$3.769 \times 10^{-7}$	0.0808	$4.948 \times 10^{-7}$	0.1061
4	$4.777 \times 10^{-7}$	0.1025	$5.648 \times 10^{-7}$	0.1211
6	$6.822 \times 10^{-7}$	0.1463	$7.832 \times 10^{-7}$	0.1678

Corrosion resistance of composites depends on many factors such as alloy composition, microstructure of matrix, techniques of preparation, porosity, precipitation of intermetallics, high dislocation densities at the particle-matrix interface, the presence of interfacial reaction products and insulating reinforcements<sup>7,20,21</sup>.

In metal matrix composites reinforced with conducting materials, the presence of less conductive phase at the interface is quoted<sup>21</sup> as not providing an easier path for electron exchange for oxygen reduction and driving the anodic reaction at a higher rate. In Al6063-TiO<sub>2</sub> composites, Moreover, galvanic corrosion between the matrix, segregation of alloying elements and intermetallics formed around the reinforcement particle are

reasons for accelerated corrosion in composites. Thus, the decreased corrosion resistance in composites is believed to be due to the fact that  $\text{TiO}_2$  serve as inert electrode for proton and oxygen reduction. The formation of intermetallic precipitates such as,  $\text{Mg}_2\text{Si}$ ,  $\text{AlTi}_3$  during fabrication of composites could be another reason for increase in corrosion rates in composites<sup>22</sup>.

From Table-1 it is observed that corrosion current densities and corrosion rates of Al6063 matrix and composites increase with increase in NaCl concentration. This could be due to greater incorporation of chloride ions into the anion vacancies of the passive  $\text{Al}_2\text{O}_3$  film<sup>23</sup>. At higher concentration of chloride ions, greater corrosion rate is observed both in matrix and composites as a consequence of preferential absorption/penetration ability of chloride ion into the passive oxide layer. Further physical examinations of the samples revealed the presence of large number of pits in composites as compared to matrix which can be attributed to increased area of reinforcements in composites<sup>18</sup> and greater degree of coupling between the products at matrix-reinforcement interface.

Scanning electron micrograph images of matrix alloy and reinforcement  $\text{TiO}_2$  are shown in Figs. 2 and 3, respectively. The particle size of reinforcement  $\text{TiO}_2$  is *ca.* 100 nm as observed in the SEM image. Following the immersion and polarization studies samples were subjected to SEM analysis after usual pretreatment. The scanning electron micrograph images of polarized samples of Al 6063 matrix alloy and its  $\text{TiO}_2$  composites are shown in Fig. 4.

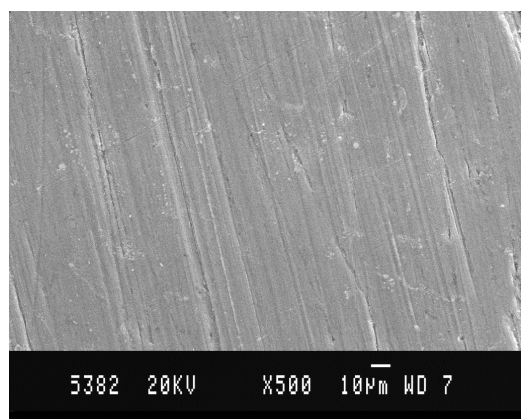


Fig. 2. Scanning electron micrograph of Al6063 matrix alloy

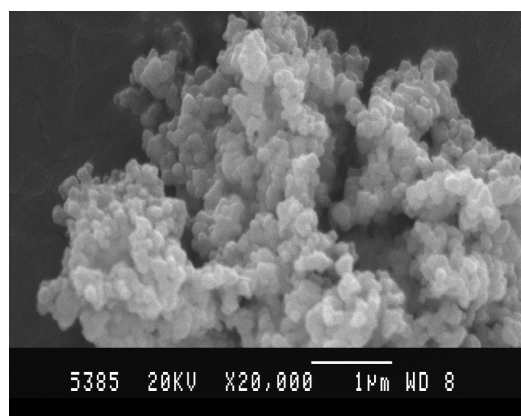


Fig. 3. Scanning electron micrograph of reinforcement  $\text{TiO}_2$

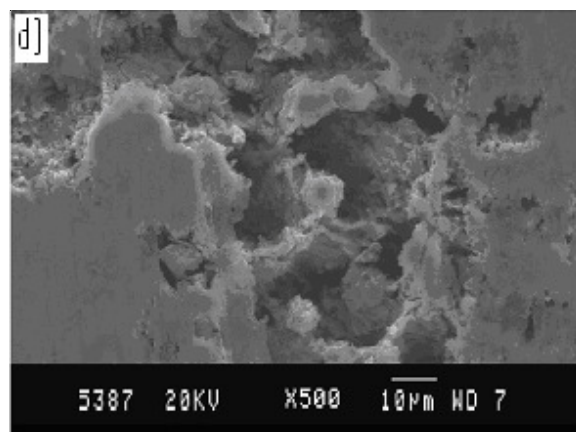
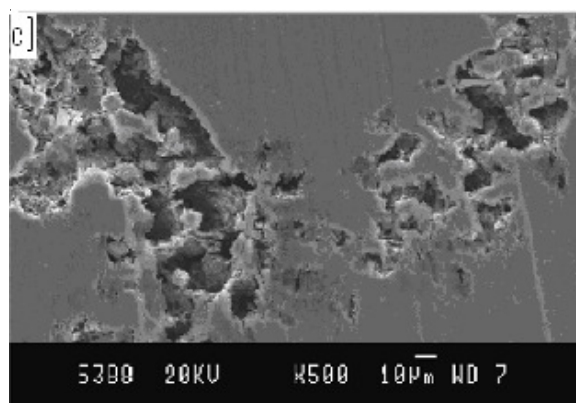
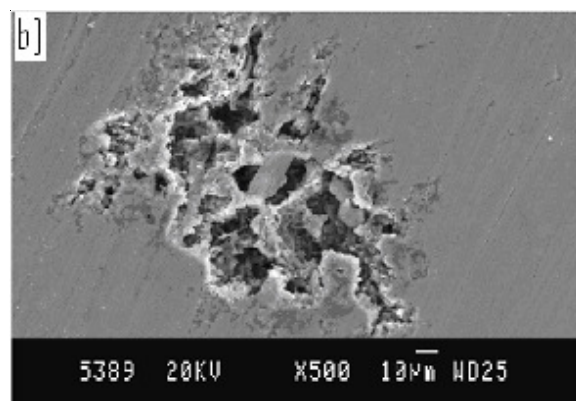
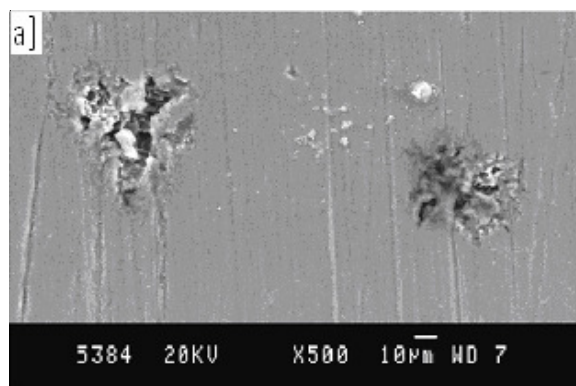


Fig. 4. Scanning electron micrographs of samples in 0.1 N NaCl [a] SEM of Al6063/0 %  $\text{TiO}_2$  matrix alloy, [b] SEM of Al6063/2 %  $\text{TiO}_2$  matrix alloy, [c] SEM of Al6063/4 %  $\text{TiO}_2$  matrix alloy, [d] SEM of Al6063/6 %  $\text{TiO}_2$  matrix alloy

The scanning electron micrographs of corroded samples of matrix and composites reveal severe pitting and cracks development in reinforced composites than unreinforced matrix alloy. Increased surface deterioration in composites as observed from SEM images indicates the higher corrosion rates for composites than matrix alloy. The SEM micrographs, show a complete deterioration of smoothness of surface of matrix<sup>24</sup> suggesting the penetration of chloride ions in to the material surface forming corrosion spots.

EDX analysis of corroded samples of Al matrix alloy and composites are shown in Fig. 5. The peak due to Al, Mg and Si is more enhanced in the reinforced composites while it decreased for matrix alloy. The presence of large amounts of aluminum in the corrosion products formed on the samples of Al composites confirms the decreased corrosion resistance in Al composites with increase in the TiO<sub>2</sub> content.

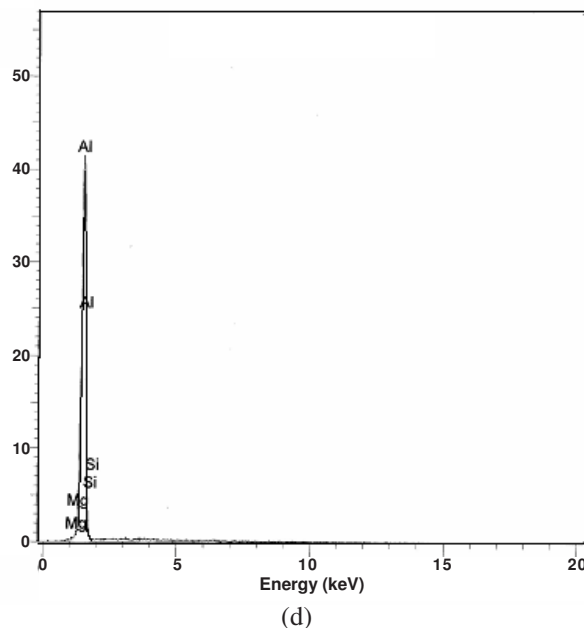
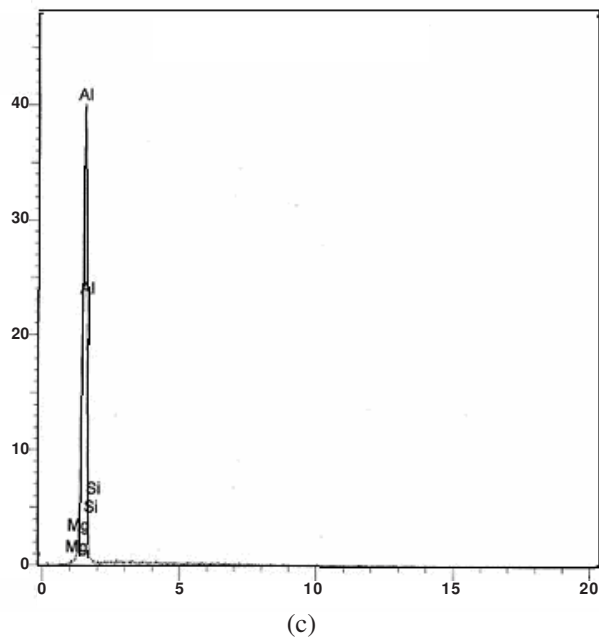
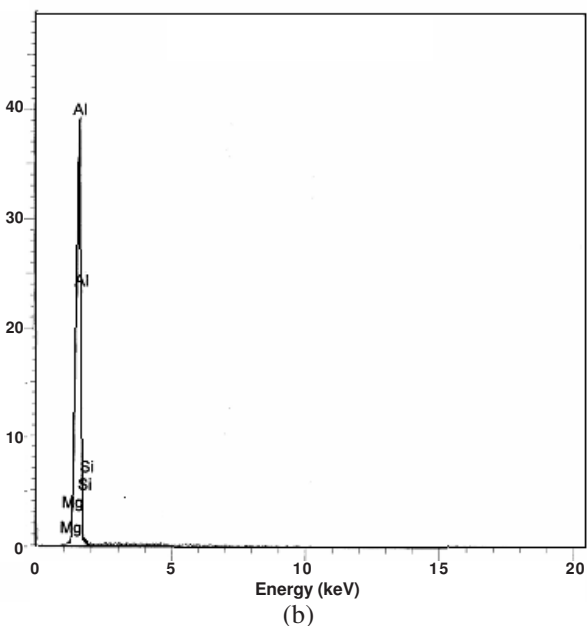
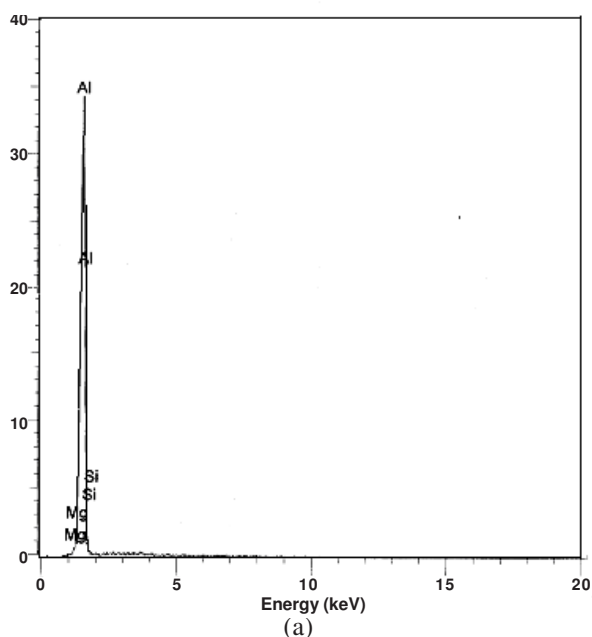


Fig. 5. EDX examinations for Al6063 matrix and its TiO<sub>2</sub> [2, 4 and 6 %] composites

Typical polarization curves for Al matrix and composites containing 2, 4 and 6 % by weight of TiO<sub>2</sub> composites in 0.1 N and 0.5 N NaNO<sub>3</sub> media exhibited the same trend as that of NaCl solution (hence not reproduced here). Table-2 gives the electrochemical corrosion parameters for the samples in 0.1 N and 0.5 N NaNO<sub>3</sub>.

Chloride ions are more aggressive in pitting due to their absorbability on the passive layer compared to nitrate ions<sup>25</sup>. The adsorption of chloride leads to the breakdown of protective oxide film<sup>26</sup> and TiO<sub>2</sub>/Al6061 interface provides preferred sites for breakdown of the protective oxide layer. Low corrosion rates observed in nitrate medium, for matrix as well as composites can be attributed to their ability to suppress both cathodic and anodic currents<sup>27</sup>. A comparison of the results indicates

TABLE-2  
ELECTROCHEMICAL CORROSION PARAMETERS OF  
Al6063 AND ITS TiO<sub>2</sub> COMPOSITES IN 0.1 N NaNO<sub>3</sub>  
AND 0.5 N NaNO<sub>3</sub> SOLUTIONS

Composite (% TiO <sub>2</sub> )	0.1 N NaNO <sub>3</sub>		0.5 N NaNO <sub>3</sub>	
	I <sub>corr</sub> (Acm <sup>-2</sup> )	Corrosion rate (mils per year)	I <sub>corr</sub> (Acm <sup>-2</sup> )	Corrosion rate (mils per year)
0	0.841×10 <sup>-7</sup>	0.0181	2.643×10 <sup>-7</sup>	0.0500
2	1.282×10 <sup>-7</sup>	0.0275	4.325×10 <sup>-7</sup>	0.0927
4	2.735×10 <sup>-7</sup>	0.0587	6.529×10 <sup>-7</sup>	0.1400
6	3.158×10 <sup>-7</sup>	0.0677	9.512×10 <sup>-7</sup>	0.1963

that the relative degree of corrosion in different ionic species follows the order Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup>. Corrosion rates and I<sub>corr</sub> values for both matrix and composites increase with increase in concentrations of chloride and nitrate media.

### Conclusion

The corrosion behaviour of unreinforced Al6061 matrix and TiO<sub>2</sub> particulate-reinforced composites (2, 4 and 6 % by weight) in NaCl and NaNO<sub>3</sub> media has been investigated using potentiodynamic polarization technique.

Results of present investigation point to the following:

(i) Corrosion current values (I<sub>corr</sub>) increases with increase in TiO<sub>2</sub> content in the composites up to 6 % by weight. This indicates a nominal increase in the corrosion rate of the matrix alloy upon reinforcement with TiO<sub>2</sub>. (ii) The decreased corrosion resistance in composites is believed to be due to the possible microgalvanic coupling between the conducting interfacial products and matrix alloy. (iii) A comparison of the corrosion parameters of the matrix alloy and its composites in chloride and nitrate media show that the corrosion rate is highest in chloride and least in the nitrate medium due to the ability of nitrate ions to suppress both anodic and cathodic currents. (iv) The scanning electron micrographs of corroded samples of matrix and composites reveal severe pitting and cracks development in reinforced composites than unreinforced matrix alloy. (v) EDX analysis of corroded samples confirms the decreased corrosion resistance in Al composites with increase in the TiO<sub>2</sub> content.

### ACKNOWLEDGEMENTS

The authors are grateful to the Principal, the Director & the Managements of Dr. Ambedkar Institute of Technology and RNS Institute of Technology, Bangalore for their support and encouragement towards the research work.

### REFERENCES

1. J.E. Allison and G.S. Cole, *J. Met.*, **45**, 19 (1993).
2. C.G.E. Mangin, J.A. Isaacs and J.P. Clark, *J. Met.*, **48**, 49 (1996).
3. H.G. Kang, D.L. Zhang and B. Cantor, *J. Microstr.*, **169**, 239 (1993).
4. M.S.N. Bhat, M.K. Surappa and S. Nayak, *J. Mat. Sci.*, **26**, 4991 (1991).
5. S.L. Pohlman, *Corrosion*, **34**, 156 (1978).
6. P.P. Trzaskoma, E. McCafferty and C.R. Crowe, *J. Electrochem. Soc.*, **130**, 1804 (1983).
7. A. Albitar, A. Contreras, M. Salazar and J.G. Gonzalez-Rodriguez, *J. Appl. Electrochem.*, **36**, 303 (2006).
8. J.B. Fogangolo, M.H. Robert, Ruiz-Navas and J.M. Torralba, *J. Mat. Sci.*, **39**, 127 (2004).
9. K.H.W. Seah, M. Krishna, V.T. Vijayalashmi and J. Uchil, *Corros. Sci.*, **44**, 917 (2002).
10. S.C. Sharma, *Corros. Sci.*, **43**, 1877 (2001).
11. P.V. Krupakara, S. Manjunatha, M. Krishna and J. Uchil, In Proceedings of Third International Conference on Advances in Composites, ADCOMP-2000, Bangalore, pp. 24-26 (2000).
12. S.C. Sharma, K.H.W. Seah, B.M. Sathish and B.M. Girish, *Corros. Sci.*, **39**, 2143 (1997).
13. A.A. Mazhar, W.A. Badawy and Abou-Romia, *Surface Coating Technol.*, **29**, 335 (1986).
14. P.L. Cabot, F.A. Centellas, J.A. Garrido, E. Perez and H. Vidal, *Electrochim. Acta*, **36**, 179 (1991).
15. W.M. Carroll and C.V. Breslin, *Br. Corros. J.*, **26**, 255 (1991).
16. J.M.G. De Salazar, S. Urena, Manzanedo and Barrena, *Corros. Sci.*, **41**, 529 (1991).
17. T. Das, P.R. Munroe and S. Bandyopadhyay, *J. Mater. Sci.*, **31**, 5351 (1996).
18. H.C.A. Murthy and V.B. Raju and H.B. Lokesh, *Mater. Sci., An Indian J.*, **4**, 328 (2008).
19. I. Gurrappa and V.V.B. Prasad, *Mater. Sci. Technol.*, **22**, 115 (2006).
20. Z.S. Liu, B.T. Wu and M.Y. Gu, *J. Mater. Sci.*, **42**, 5736 (2007).
21. J. Bienias, M. Walczak, B. Surowska and J. Sobczak, *J. Optoelectron. Adv. Mater.*, **5**, 493 (2003).
22. P.P. Trzaskoma and E. McCafferty, Aluminium Surface Treatment Technology, The Electrochemical Society, Pennington, NJ, p. 171 (1986).
23. Z. Szklarska-Smialowska, *Corros. Sci.*, **41**, 1743 (1999).
24. J. Datta, C. Bhattacharya and S. Bandyopadhyay, *Bull. Mater. Sci.*, **28**, 253 (2005).
25. L. Tomcsanyi, K. Varga, I. Bartik, G. Horanyi and E. Maleczki, *Electrochim. Acta*, **34**, 6855 (1989).
26. J. Datta, B. Samantha, A. Jana, S. Sinha, C. Bhattacharya and S. Bandyopadhyay, *Corros. Sci.*, **50**, 2658 (2008).
27. Z. Ahmad, P.T. Paulette and B.J.A. Aleem, *J. Mater. Sci.*, **35**, 2573 (2000).