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A study on the effect of TiO₂ particulate reinforcement on corrosion behaviour of Al-6063 based composites

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ABSTRACT

The corrosion behaviour of Al 6063 alloy- TiO₂ particulate composites have been studied in the present investigation, in acidic and alkaline media. The unreinforced matrix, as well as the composites containing 2, 4 and 6% by weight of TiO₂ particulates were prepared by liquid metallurgy route using vortex technique and their corrosion behaviour was evaluated by weight loss method and galvanostatic polarisation methods. The corrodents used were 1N HCl, 1N NaCl, 1N NaOH. and equimolar mixture of 1N NaOH and 1N NaCl. The highest corrosion rate was observed in the case of corrodent 1N NaOH. The rate of corrosion of both the matrix alloy and the composites decreased with increase in time of exposure in various media. When TiO₂ is added to matrix, it exhibits insulator action towards corrosion medium and thereby reduces the percentage of pits and cracks formation. The Icorr values of Al6063 Matrix alloy and Al6063/TiO₂ composites were found to decrease as the TiO₂ content increased from 0% to 6% in all media, which could be attributed to particulates acting as physical barrier to the initiation and growth of pits during corrosion. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Al 6063 alloy- TiO₂ particulate composites;
Vortex technique;
Polarisation methods;
Insulator action;
Pits and cracks;
Icorr values.

1. INTRODUCTION

Aluminium composites with their unique thermal properties such as metallic conductivity with co-efficients of expansion that can be tailored down to zero, have enormous prospects in space and avionics sectors. Al-matrix composites have the potential of achieving significant weight and cost savings on aircraft structures.

Because of their low density and good mechanical properties, aluminium matrix composite materials have recently been proposed as alternative structural mate-

rials to conventional aluminium alloys. However, the presence of reinforcing particles in the metal matrix, such as Al₂O₃, SiC, and graphite, can increase the inhomogeneity of the alloy microstructure and subsequently affect the susceptibility of the metal matrix composite (MMC) to localised corrosion.

The corrosion behaviour of the MMC is affected by several factors: composition of the metal matrix, its porosity, nature of the reinforcing material and the precipitation of intermetallic phases within the matrix, such as Cu-Al intermetallic compounds which act as cath-

ode with respect to the matrix resulting in promotion of localised corrosion. Trzaskoma^[1], reported that the pitting potential, E_p values were matrix alloy dependent, rather than reinforcement dependent. It was also understood that the rate of corrosion in fibre reinforced MMCs is faster than the particulate MMCs. Exposure of SiC fibres in Al 6061- SiC resulted in the enhancement of corrosion rate in composite relative to the matrix^[2].

Ramanathan^[3], reported the effect of SiC particle characteristics such as its composition, volume fraction and pre-treatment on the aqueous corrosion behaviour of Al - MMCs. Sharma^[4] investigated the stress corrosion behaviour of Al6061/albite composite in higher temperature acidic medium using autoclave. The corrosion rate decreases with increasing percentage of albite reinforcement. The material loss from corrosion was significantly higher in the case of pure Al than in the reinforced alloys. Similar decrease in corrosion rate has been reported for for both the unreinforced matrix LM13 alloy and the composites reinforced with garnet and albite by Seah et al^[5,6]. Studies^[7] on ZA-27/ glass- fibre composites also show decrease in the corrosion rate with increase in glass- fibre content.

The corrosion behaviour of Al6061 and Al7005 reinforced with Al_2O_3 particles in aerated 3.5% chloride solution was studied by De Salazar^[8]. The pitting corrosion mechanisms for Al6061 MMCs reinforced with alumina particles are affected by the heat treatments given. Zaki Ahmed^[9], reported the corrosion behaviour of Scandium alloyed Al5052 in neutral sodium chloride solution. The corrosion studies were divided into two parts; weight loss studies and electrochemical studies. The weight loss studies conducted in 3.5 wt% NaCl showed that the corrosion rate decreased with increased exposure period. Pardo^[10] investigated the effect of reinforcement coating on corrosion behaviour of AA6061/SiC/20 composite in high relative humidity environments. SiC particle reinforced Al6061 composites^[11] were found to corrode faster than the base alloy even though the attack was mainly confined to the interface, resulting in crevices or pits.

For Al6061 composites with particulate TiO_2 a decrease in corrosion resistance as compared with the matrix alloy, has been reported by Ramesh et al.^[12].

The present investigation involves the study of the

effect of addition of TiO_2 particulate reinforcement on corrosion behaviour of Al-6063 based composites.

In the present paper, Al-6063 alloy and its composites containing different weight percentages of reinforcement, TiO_2 are fabricated by liquid metallurgy technique and their electrochemical corrosion behaviour was studied by immersion tests in chloride and hydroxide media.

The studies include galvanostatic anodic and cathodic polarization characteristics of Al-6063/ TiO_2 MMCs.

EXPERIMENTAL

Materials selection

Aluminium alloy 6063 -Matrix

Aluminium alloy 6063 had the composition: Si -0.2 to 0.6%, Fe -0.35%, Cu- 0.1%, Mn- 0.1%, Mg- 0.45 to 0.9%, Zn, Cr, Ti- 0.1% each and remaining Al. The alloy was of ASTM standards.

Reinforcement

TiO_2 , 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. Addition of reinforcement material TiO_2 in to the molten Al-6063 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 zinc alloy). The stirrer(Figure 1) was rotated at a speed of 450 rpm in order to create the necessary vortex. The TiO_2 particles were pre-heated to 400°C and added in to the vortex of liquid



Figure 1: Electrical furnace

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Figure 2: Al6063/TiO₂ composites in the form of cylindrical rods

melt at a rate of 120 g/min. The TiO₂ particulates were of size varying 50 - 80 μm. The weight percentage of TiO₂ used was 2-6 in steps of 2%. The composite melt was thoroughly stirred and subsequently degasifiers were added. Castings were produced in permanent moulds in the form of cylindrical rods (Figure 2). [Diameter 30 mm and length 150 mm].

Specimen preparation

Casted material was cut into 20×20 mm pieces using an abrasive cutting wheel. The matrix alloy was also cast under identical conditions for comparison. The samples were successively ground using 240, 320, 400 and 600 SiC paper and were polished according to standard metallographic techniques and degreased in acetone and dried. The samples were weighed up to fourth decimal place using electronic balance and also the specimen dimensions were noted down using Vernier gauge.

For galvanostatic test, the composites and the pure alloy matrix were cut into rectangular shaped specimens of 2 cm length, 1 cm width and 1 mm thickness and made ready as described above and dimensions were noted down using Vernier gauge.

Corrosion test

(A) Weight loss method

The corrosion behaviour of Al-6063 alloy was studied by static immersion test to measure the material loss.

Weight loss measurements were carried out by weighing pure Al6063 alloy and the composite specimens before and after immersion in 200 ml solutions (of 1N HCl, 1N NaCl, 1N NaOH and Equinormal mixture of NaOH and NaCl). Samples were suspended in the corrosive medium for different time intervals up to 96 hours in steps of 24 hrs. After the specified time

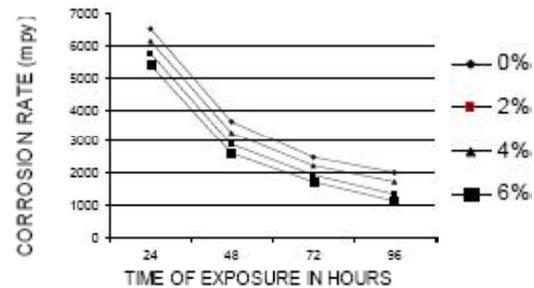


Figure 3 : Corrosion rate of composites with different percentages TiO₂ (2%, 4% & 6%) in 1N HCl

the samples were cleaned mechanically using a brush to remove the heavy corrosion deposits on the surface. At least three samples were tested and average value of the weight loss was determined. Corrosion rates were computed using the equation given below.

$$\text{Corrosion rate} = 534 W / DAT \text{ mpy}$$

Where W is the weight loss in mg, D is density of the specimen g/cm³, A is the area of the specimen sq-inch and T is the exposure time in hours.

(B) Galvanostatic method

Corrosion cell was set up with

- Working electrode (Sample)
- Reference electrode (SCE)
- Counter electrode (Pt electrode)

The corrosion cell was connected to the circuit and the electrolyte was stirred mildly by magnetic stirrer, the rest potential also referred to as open circuit potential was noted down after an equilibration time of one hour. The anodic and cathodic polarization values were measured under galvanostatic conditions using digital potentiostat (ELICO). The applied current was varied between 1 and 100 amperes.

RESULTS AND DISCUSSIONS

(A) Weight loss tests

Corrosion rate of composites with different percentages of TiO₂ (2%, 4%, 6%) in 1N HCl solution is shown in figure 1. Figure 2 gives the corrosion rate of composites with different percentages of TiO₂ in 1N NaOH. Figure 3 gives the corrosion rate of composites with different percentages of TiO₂ in equinormal mixture of 1N NaOH and 1N NaCl. Figure 4 gives the corrosion rate of composites with a different percentages of TiO₂ in 1N NaCl.

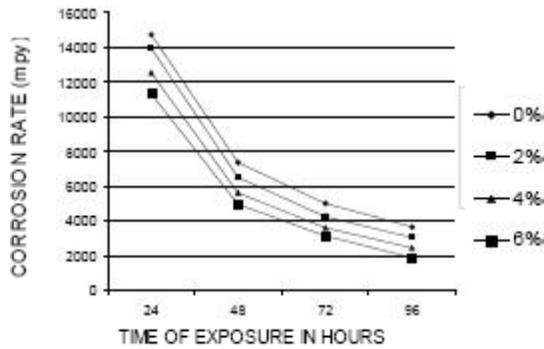


Figure 4 : Corrosion rate of composites with different percentages TiO₂ (2%, 4% and 6%) in 1 N NaOH

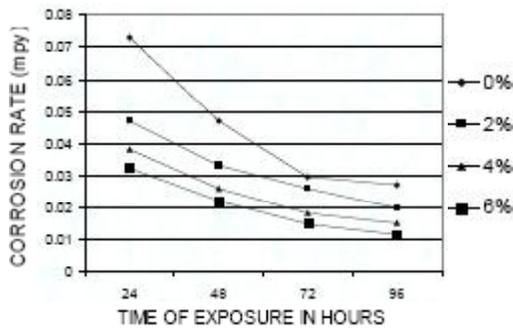


Figure 5 Corrosion rate of composites with different percentages TiO₂ (2%, 4% and 6%) IN mixture of 1N NaOH and 1N NaCl

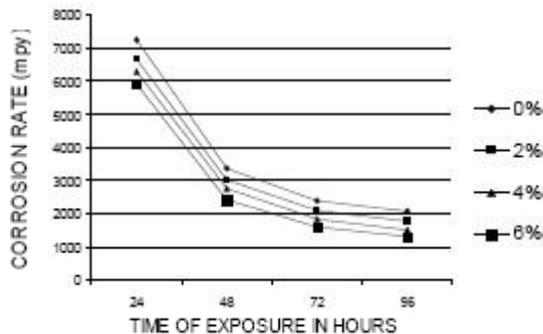


Figure 6 : corrosion rate of composites with different percentages TiO₂ (2%, 4% and 6%) 1N NaCl

Effect of test duration

The corrosion rate (mpy) is measured as a function of exposure time in the static immersion test as shown in the figures 3-6*. Corrosion rate decreases from 0 to 96 hours. It can be observed that corrosion resistance of the composites also increases with increase in exposure time. This decrease in corrosion rate is the indication of possible passivation of matrix alloy.

*The values of corrosion rate expressed as mpy are summarised in TABLES 1, 2, 3 and 4.

TABLE 1: Weight loss corrosion test in 1N HCl

% Reinforcement	Exposure time in hours			
	24	48	72	96
0	14766	7354	5020	3660
2	13931	6508	4263	3050
4	12530	5632	3600	2440
6	11350	4970	3140	1920

TABLE 2: Weight loss corrosion test in 1N NaOH

% Reinforcement	Exposure time in hours			
	24	48	72	96
0	6553	3620	2500	2030
2	5760	2910	1970	1350
4	6130	3282	2255	1735
6	5400	2620	1740	1150

TABLE 3: Weight loss corrosion test in 1N NaOH + 1N NaCl

% Reinforcement	Exposure time in hours			
	24	48	72	96
0	7255	3370	2380	2060
2	6668	3000	2090	1770
4	6299	2743	1830	1510
6	5901	2400	1600	1290

TABLE 4: Weight loss corrosion test in 1N NaCl

% Reinforcement	Exposure time in hours			
	24	48	72	96
0	0.072	0.0469	0.0296	0.027
2	0.047	0.033	0.026	0.0199
4	0.038	0.0259	0.0182	0.0152
6	0.023	0.0222	0.0149	0.0117

Effect of TiO₂ content

Corrosion rate decreases monotonically with an increase in TiO₂ content. In the absence of the reinforcement (TiO₂ - 0%), the presence of visible cracks and pits was observed clearly on the base alloy surface. Since there is no reinforcement provided in any form the base alloy fails to provide any sort of resistance to the acidic medium. Hence weight loss in case of unreinforced alloy is higher than that of composites. When TiO₂ is added to matrix, it exhibits insulator action towards corrosion medium and thereby reduces the percentage of pits and cracks formation.

Of all the corrosion media investigated, the highest corrosion rate was observed in the case of corrodent 1N NaOH. In the case of equimolar mixture of 1N NaOH and 1N NaCl, the rate of corrosion is little lesser in comparison with corrodent 1N NaOH.

B. Galvanostatic tests

Figure 7 show the Anodic and Cathodic Polarisation curves for Al6063/TiO₂ MMC that are typical for both

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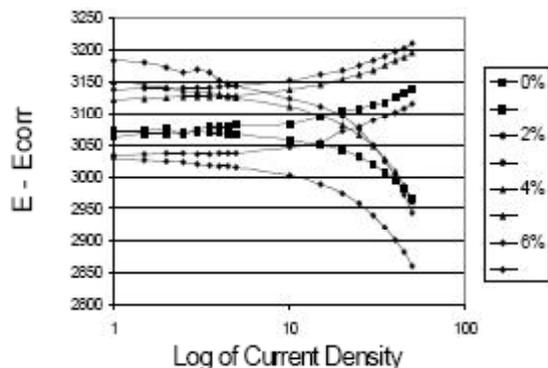


Figure 7: Mixed polarization curves for Al 6063 (0%, 2%, 4% & 6% TiO₂) composites in 1N NaOH

composite and matrix alloy in 1N NaOH solution. To determine the effect of normality on the corrosion current density (I_{corr}), electrochemical Galvanostatic measurements were carried out in 0.25 N NaOH, 0.5 N NaOH, 1N NaOH and a mixture of 1N NaOH and 1N NaCl solutions. It was found from the I_{corr} values that a decrease in concentration of the solutions results in marked decrease in corrosion rate for both composite and matrix alloy.

Effect of TiO₂

The I_{corr} values from the galvanostatic polarization curves were found to decrease with increase in the content of TiO₂ in the composites [2%, 4% and 6%]. These results corroborate the results from weight loss tests that, the corrosion resistance of composites increases with increase in the percentage of TiO₂. This confirms the fact that the TiO₂ particulates do influence the corrosion characteristics of the composites. Aluminium alloy with TiO₂ reinforcement possess high hardness and modulus, and is predicted to have superior corrosion resistance^[14]. Our observation of increased corrosion resistance by TiO₂ differs from that reported for Al6061-TiO₂ composite where a deterioration of corrosion resistance when compared to the matrix alloy has been observed.

Effect of concentration of NaOH

The I_{corr} values were found to increase with increase in concentration from 0.25N to 1N NaOH.

Anodic and Cathodic polarisation curves for both matrix alloy and reinforced composites are similar in nature with slight changes in the absolute values of corrosion current density.

TABLE 5: Galvanostatic anodic and cathodic polarisation of (Al 6063 + 0%TiO₂)

Current I in amp	Potential E in mv		E - E _{CORR}	
	Anodic	Cathodic	Anodic	Cathodic
1	1496	1515	3053	3072
2	1505	1514	3062	3071
3	1509	1517	3066	3074
4	1510	1510	3067	3067
5	1511	1516	3068	3073
6	1512	1520	3069	3077
7	1511	1521	3068	3078
8	1511	1497	3068	3054
9	1510	1523	3067	3080
10	1510	1524	3067	3081
20	1490	1537	3047	3094
30	1493	1545	3050	3102
40	1484	1551	3041	3108
50	1473	1556	3030	3113
60	1462	1564	3019	3121
70	1450	1569	3007	3126
80	1439	1575	2996	3132
90	1425	1580	2982	3137
100	1408	1586	1965	3141

Rest Potential (E_{CORR}) = 1557 mv

TABLE 6: Galvano static anodic and cathodic polarisation of (Al 6063 + 2%TiO₂)

Current I in amp	Potential E in mv		E - E _{CORR}	
	Anodic	Cathodic	Anodic	Cathodic
1	1532	1531	3034	3033
2	1527	1532	3029	3034
3	1524	1533	3026	3035
4	1523	1534	3025	3036
5	1520	1534	3022	3036
6	1517	1533	3019	3035
7	1516	1533	3018	3035
8	1515	1535	3017	3037
9	1514	1535	3016	3037
10	1513	1536	3015	3036
20	1500	1544	3002	3046
30	1486	1552	2988	3054
40	1472	1569	2974	3071
50	1456	1576	2958	3078
60	1438	1587	2940	3089
70	1419	1592	2921	3094
80	1399	1599	2901	3101
90	1380	1605	2882	3107
100	1357	1613	2859	3115

Rest Potential (E_{CORR}) = 1557 mv

The intensity of corrosion attack increases with increasing concentration of NaOH. Formation of intermetallic precipitates has been found to occur which provides an easier path for the electron exchange necessary for reduction^[15]. A higher corrosion rate was due to the availability of hydroxyl ion from alkali. A higher number of corrosion pits were observed on the matrix

TABLE 7: Galvanostatic anodic and cathodic polarisation of (Al 6063 + 4%TiO₂)

Current I in amp	Potential E in mv		E - E _{CORR}	
	Anodic	Cathodic	Anodic	Cathodic
1	1598	1561	3155	3118
2	1592	1565	3149	3122
3	1588	1566	3145	3123
4	1584	1568	3141	3125
5	1579	1569	3136	3126
6	1577	1569	3134	3126
7	1575	1569	3132	3126
8	1573	1570	3130	3127
9	1569	1570	3126	3127
10	1567	1571	3124	3128
20	1553	1580	3110	3137
30	1537	1588	3094	3145
40	1524	1596	3081	3153
50	1508	1603	3065	3160
60	1490	1610	3047	3167
70	1471	1618	3028	3175
80	1451	1625	3008	3182
90	1429	1631	2986	3188
100	1405	1638	2962	3195

Rest Potential (E_{CORR}) = 1557 mv**TABLE 8: Galvanostatic anodic and cathodic polarisation of (Al 6063 + 6%TiO₂)**

Current I in amp	Potential E in mv		E - E _{CORR}	
	Anodic	Cathodic	Anodic	Cathodic
1	1611	1559	3188	3136
2	1606	1560	3183	3137
3	1597	1561	3203	3138
4	1590	1562	3196	3139
5	1586	1563	3163	3140
6	1582	1563	3168	3140
7	1578	1564	3164	3141
8	1575	1565	3152	3142
9	1570	1566	3147	3143
10	1567	1566	3144	3143
20	1546	1575	3123	3152
30	1534	1583	3111	3160
40	1517	1590	3094	3167
50	1497	1598	3074	3175
60	1473	1605	3050	3182
70	1448	1612	3025	3189
80	1424	1619	3001	3196
90	1396	1625	2973	3202
100	1368	1632	2945	3209

Rest Potential (E_{CORR}) = 1557 mv

alloy than on the composites. It was also observed that Al6061 / SiC_p composites suffers localised corrosion^[13] in acid medium Corrosion behaviour is closely associated with the presence of heterogeneities and MMC's have large quantities of heterogeneities in the form of reinforcement, microcrevices, voids, porosity, second phase precipitates and interaction products. This may

be due to increased coverage of reinforcement on the composites. Particulates act as inert barriers to the initiation and development of pitting corrosion, modifying the micro structure and hence improving the corrosion resistance.

CONCLUSIONS

Through the present investigation, it has been established that:

1. Al6063/TiO₂ composites can be prepared by the addition of TiO₂
2. Particles in molten Al6063 alloys by vortex method followed by casting in suitable permanent moulds.
3. It is possible to introduce only preheated TiO₂ particles (temperature of 400°C) to obtain a uniform dispersion of TiO₂ particulates on a macroscopic scale
4. Corrosion rates of Al6063/TiO₂ composites decrease as a function of time of exposure in 1N HCl, NaCl, NaOH and mixtures of NaOH and NaCl solution.
5. Of all the corrosion media investigated, the highest corrosion rate is observed in the case of corrodent 1N NaOH. Icorr values increase with increase in the concentration of the corrodent, NaOH for both matrix alloy as well as composites.
6. Corrosion current density, Icorr values of pure Matrix alloy and the composites decrease as the TiO₂ content increases (0 to 6%) in various concentrations of NaOH solution.
7. The corrosion rate of the composites was always lower than that of the corresponding matrix alloy.

It can be conclusively stated that TiO₂ in Al6063 alloys play a significant role in the corrosion resistance of the composite materials. Increase in the percentage of TiO₂ aids in reducing the density and increasing the corrosion resistance significantly.

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