CORROSION BEHAVIOUR OF AS SINTERED P/M Al-SiC COMPOSITES

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Metal matrix composites based on aluminium alloy matrices are widely being used for structural applications. Though these composites are made by both liquid metallurgy and powder processing routes, the corrosion resistance of these materials is still not well understood. In the present study, an attempt has been made to produce composites consisting of commercial pure aluminium (99%) and silicon carbide particles by the powder metallurgy route and characterize their corrosion behaviour in the as sintered condition in 3.5% NaCl solution of varying pH levels. Results of the study indicate that the composites in the as sintered state have better corrosion resistance than the monolithic material.

Keywords: Composites, Aluminium, Silicon carbide and corrosion.

INTRODUCTION

Ceramic particle reinforcements are now increasingly being used to strengthen light weight materials such as aluminium and magnesium alloys to produce high strength and wear resistance composites for specific applications. These composites have excellent structural and tribo-mechanical properties, good thermal and electrical conductivities and high vibration damping characteristics. Therefore, there is an increasing tendency in industries, especially that of automotive, aeronautical and defence, to use these materials for heavy duty applications and in critical components. A potential factor for caution, however, is their doubtful corrosion resistance due to their heterogeneous composition. Recent reports in literature on these aspects are not very encouraging for their wider acceptability. Production and post production oriented treatments of composites have been reported to cause drastic physical and chemical changes at the matrix/particle interface, depending on the nature of the particle and treatment [1]. Generation of conducting reaction products and micro-segregation of elements and compounds are some of the chemical changes occurring at the interface formation The physical changes include microcrevices, voids and porosites [3]. These changes, therefore, introduce intense galvanic and crevice effects at the interface, which may lead to the worsening of their corrosion resistance [4].

Various methodologies have been introduced recently to mitigate the above mentioned deleterious effects. Cladding of metal sheets, anodising, spray deposition of metals, control of processing parameters and particle pretreatment are some of the important methods [5]. In the present study, an attempt has been made to produce composites containing silicon carbide particles in commercial pure aluminium matrix in the powder processing route, characterize their corrosion behaviour and establish the fact that the controlled composition, production and treatment may eliminated the intrinsic interaction between the particles and the matrix leading to the production of materials with optimum properties.

EXPERIMENTAL DETAILS

Composites containing 10-30 weight percentage silicon carbide (SiC_p) in commercial pure aluminium (99%) matrix were made by powder metallurgy route. Abrasive grade SiC_p (100-120 um) was used for this purpose. The attritor mixed dry aluminium powder and silicon carbide particles were pellatized under a compaction pressure of 97 MPa to circular discs of 30 mm diameter and 20 mm thick, using graphite as lubricant. The prepared briquettes were then sintered at 853 \pm 10 K in an inert atmosphere of dissociated

ammonia for 2 hours. The sintered composites were polished using 200, 400 and 600 grit emery sheets successively and then subjected to electrochemical studies.

Hardness measurements were made in a LECO DM 400 model Vickers micro hardness tester under a load of 500 g. Potentiodynamic polarisation studies were conducted in a three electrode cell using a potentiostat model EG & G PARC 173 in conjunction with a scanner model EG & G PARC 175 and an X-Y recorder.

Impedance measurements were made using a three electrode cell in which the calomel, platinum and the sample were the reference, auxiliary and working electrodes respectively. The experimental set-up consisted of the following.

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IBM PC

Lockin analyser	PAR 520
Potentiostat	PAR 273
Software	M 378

Lockin mode of measurements were made in the frequency range of 10 kHz - 10 Hz and the Fast Fourier Transform measurements were made in the frequency range 5 Hz - 0.1 Hz. An a.c. amplitude of 5 mV was applied during the lockin mode of measurements and 10 mV during the FFT measurements.

Samples were evaluated in a 3.5% NaCl solution of pH 7 and 11 and in 0.1 M HCl at 303 K. Analar grade chemicals were used for the preparation of test solutions.

RESULTS AND DISCUSSION

Table I shows the variation of microhardness with incorporation of SiC_p. The microhardness varies from 40-65 VPN as the incorporation level is increased from 0-30%. This increase in the hardness in attributed to the restriction imposed by the embedded SiC particles on the deformation of the matrix. Similar observations have been made by various investigators [6-7].

Metallographic observation of the prepared specimens indicate that the distribution of SiC_p in the aluminium matrix is uniform with minimum agglomeration, which is very important for good mechanical properties. No reaction products were observed in the matrix/particle interface

TABLE I: Variation of microhardness with increase in incorporation

Material	Hardness, VPN	
Pure aluminium	40	
10% composite	48	
20% composite	54	
30% composite	65	

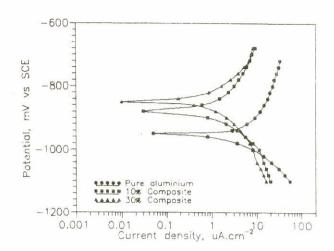


Fig. 1: Potentiodynamic polarisation behaviour of aluminium composites in 3.5% NaCl (pII = 7)

region. Absence of voids and crevices in this region indicates good mechanical bonding of the particles with the matrix.

Fig. 1 shows the polarisation behaviour of commercial pure

aluminium (99%) and its composites in 3.5% NaCl solution of pH 7 and the results are given in Table II. These data indicate that the value of corrosion current density (i_{corr}) decreases as the SiC content in the composite increases. This can be attributed to the reduction in real area of the exposed metal in the composite by the embedded SiC, which is a good electrical insulator at room temperature with its specific resistance being in the range 10^8 - 10^{10} ohm-cm.

The corrosion potential (E_{corr}) of the aluminium matrix is found to have shifted to nobler values when incorporated with SiC particles. As the incorporation level is increased in the matrix, the shift is more towards the nobler side. The corrosion potential has been shown to be a function of the standard electrode potentials E^0 , Tafel slopes and exchange current densities of both anodic and cathodic partial reactions and is related as given below [9].

TABLE II: Polarisation data for composites in 3.5% NaCl solution (pH 7)

Material	Corrosion potential (mV/SCE)	Corrosion current µA/cm²	Corrosion rate mm/y
Pure aluminium	-940	2.00	0.0218
10% composite	-880	0.35	0.0038
20% composite	-864	0.18	0.0019
30% composite	-822	0.12	0.0013

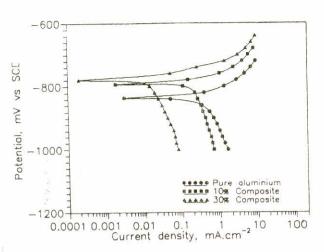


Fig. 2: Potentiodynamic polarisation behaviour of aluminium composites in 0.1 M HCl

$$E_{corr} = \frac{B_a E_c^0}{B_a + B_c} + \frac{B_c E_a^0}{B_a + B_c} + \frac{B_a B_c}{B_a + B_c} \ln \frac{i_{o,c} x A_c}{i_{o,a} x A_a}$$

It appears that the decrease in the real exposed area of the aluminium matrix causes more drastic decrease in the anodic areas than the cathodic areas, leading to ennobling of the corrosion potential of composites.

Fig. 2 shows the effect of SiC incorporation on the corrosion of aluminium matrix in 0.1 M HCl solution. In this solution, since the exchange current density for hydrogen reduction is quite higher than that for the oxygen reduction, the most predominant reaction will be that of hydrogen ion reduction [10]. It is evident that the incorporation of SiC decreases the current for the reduction of H⁺ ions considerably and the current decreases further with higher incorporation. The corrosion current densities further determined by Tafel extrapolation method are given in Table III. The decrease in the corrosion current densities and therefore the corrosion rate can be attributed to the reduction in the aluminium matrix area in the composites, as has been explained in the context of neutral sodium chloride solution. The results of

TABLE III: Polarisation data for composites in 0.1 M HCl

Material	Corrosion potential (mV/SCE)	Corrosion current $\mu A/cm^2$	Corrosion rate mm/y
Pure aluminium	-860	350	3.8157
10% composite	-845	160	1.7443
20% composite	-805	100	1.0902
30% composite	-785	55	0.5451

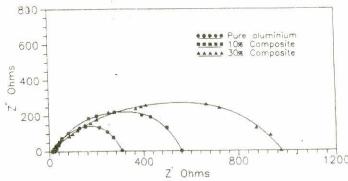


Fig. 3: Nyquist type impedance plots for the composites in 0.1 M HCl solution

the corrosion resistance measurements through impedance studies presented in Fig. 3 also corroborate the above fact. The shift in the corrosion potential of the composites is much towards the nobler side than that has been observed in 3.5% NaCl solution of pH 7 and can be explained by the same relation given in the earlier part.

The results of the single cycle potentiodynamic anodic polarisation studies are presented in Fig. 4. The passivation current densities (i_p) and the pitting potentials (E_p) determined from the plots are given in Table IV. As can be seen, the composites show an overall improvement in the above parameters.

The passivation current density reduces as the incorporation of SiC in the aluminium matrix increases. The pitting potentials for the composites are also higher when compared to monolithic aluminium and it increases with incorporation. By now it is well understood that the SiC_p reduces the real exposed area of the aluminium matrix in the composites,

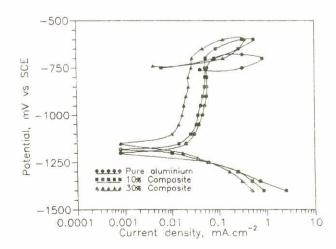


Fig. 4: Potentiodynamic polarisation behaviour of composites in 3.5% NaCl solution (pH = 11)

TABLE IV: Polarisation data for composites in 3.5% NaCl solution (pH = 11)

Material	Corrosion potential (mV/SCE)	Pitting potential (mV/SCE)	Protection potential (mV/SCE)	Passive current (μA/cm²)
A	-1200	-740	-800	50
B	-1180	-680	-710	35
C	-1175	-680	-715	25
D	-1150	-675	-715	18

A = Pure aluminium;

B = 10% composite

C = 20%composite

D = 30% composite

while the apparent area remains the same. Therefore, the same applied current is able to give higher anodic current density, in the local context, for the composite than for the monolithic aluminium matrix. Therefore, the composites attain the critical current for passivation much faster than the monothic aluminium.

The shift in pitting potential (E_p) of aluminium with higher SiC content can be attributed to two prominent factors. First the SiC might have helped in nucleating more of the Al_2O_3 at the intervening regions of aluminium, thus forming more of an adherent and coherent oxide film on these regions. Secondly, the effect offered by the embedded SiC_p also might have helped in retaining the cohesiveness and tenacity of the oxide layer.

It has been shown that energetically distinguishable sites (microstructural and crystallographic defects) are the points where primary nuclei appear exclusively when oxidation occurs at low temperatures with a low cell voltage [11]. At

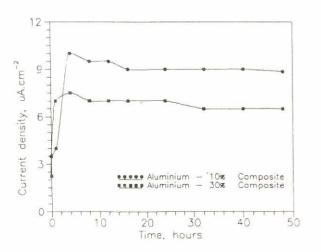


Fig. 5: Galvanic current measurements using ZRA Pure aluminium — Composite couples

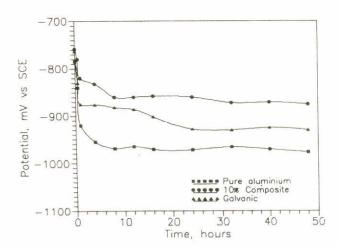


Fig. 6: Galvanic potential measurements Pure aluminium — 10% composite couple

defect-free sites, oxidation starts and progresses more slowly. Because of these two effects, the oxide layer formed on the exposed matrix region of the composites might have been thicker and defect-free than that formed on monolithic aluminium matrix. Since the penetration of adsorbed chloride ion on the weaker and defective sites of Al₂O₃ layer is assisted by the potential [12], a higher potential will be required to penetrate the thickened layer which leads to the higher pitting potential for the composites.

The bimetallic combination of composites and monolithic aluminium in 3.5% NaCl solution show some interesting results (Figs. 5, 6 and 7). As has been observed earlier, the composites show nobler potentials than monolithic aluminium in this medium. Thermodynamically such galvanic combinations of composites and aluminium are expected to produce a galvanic current, the maximum being

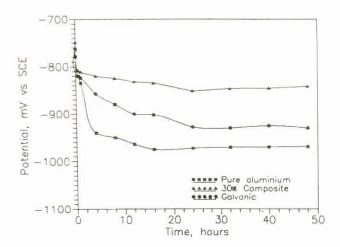


Fig. 7: Galvanic potential measurements Pure aluminium — 30% composite couple

TABLE V: Dissolution rates of aluminium in the galvanic cells; i_{corr} , $Al = 2 \mu A cm^{-2}$ Dissolution current density, $i_{d} = i_{g} + i_{corr}$, Al

Couple	Galvanic current density i µA cm ⁻²	Dissolution current density, i _d $\mu A \text{ cm}^{-2}$	Corrosion rate, r _d mm y ⁻¹
Al-10% composite	9.8	11.8	0.1286
Al-20% composite	7.5	9.5	0.1036
Al-30% composite	6.8	8.8	0.0959

expected from the cell consisting of the composite with highest incorporation of SiC. However, the experimental observations are quite contrary and the galvanic current is minimum for this couple. This can be understood by the fact that though the essential condition for the galvanic corrosion is the potential difference between the two electrodes comprising the cell, that alone is not sufficient to completely define such a form of corrosion. The kinetic parameter of exchange current is the chief controlling factor in such bimetallic combinations, as has been observed for Au-Zn and Pt-Zn couples in hydrochloric acid. Gold electrode, despite being nobler than platinum (E_{o,Au} = +1.498 V and E_{o,Pt}= +1.2 V) induces much less galvanic corrosion on zinc than the platinum electrode of similar area due to its low exchange current density (i_{o,Au}= 10⁻⁶A.cm⁻² and i_{o,Pt}= 10⁻³A.cm⁻²). The composites comprising higher amount of SiC_p with nobler potentials, have low exchange current density for oxygen reduction in the presence of more of the insulating SiC particles on the surface. The galvanic current for such cells are, therefore, much less than cells of composites with low SiC content. The initial smaller values for the galvanic current densities as observed in Fig. 5 are due to the time taken by the electrodes to attain their full potential values as given in Figs. 6 and 7. The real corrosion rates of aluminium in galvanic cells, i_{d.Al} (uA.cm⁻²) and r_{d Al} (mm.y⁻¹) can be determined using the relation given below [14] and the results are presented in Table V.

$$i_{d,Al} = i_g + i_{corr,Al}$$

where ig is the average galvanic current density and icorr, Al is the corrosion current density for monolithic aluminium.

It therefore appears that the composite with maximum SiC content in the matrix is much safer with respect to galvanic corrosion in similar situations.

CONCLUSIONS

Composites of Al-SiC_p, processed by powder metallurgy route with optimum processing conditions so as to cause minimum reaction between the two phases, show very good corrosion resistance characteristics. The composites retained their corrosion resistance in both acidic and neutral chloride solutions and the pitting tendencies of such composites are also much less marked than monolithic aluminium in chloride media. Contrary to the belief, the composites containing higher SiC content induced much less galvanic corrosion of monolithic aluminium, thus underlining the importance of controlled processing of composites for safer applications.

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