

AQUEOUS CORROSION BEHAVIOR OF PARTICLE REINFORCED ALUMINIUM BASE
METAL MATRIX COMPOSITES

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ABSTRACT

The aqueous corrosion behavior of SiC or Alumina particle reinforced Al alloy base composites obtained by stir casting has been studied. Electrochemical and immersion tests in 3.5% NaCl solutions have been carried out to verify the influence of the matrix alloy, particle parameters such as size, content and pretreatment as well as anodization of the composite on the corrosion behavior. The corrosion potential varied with aeration of the electrolyte and the pitting potential upon addition of SiC. Increased pitting of the composites is due to the availability of a large number of initiation sites in the form of the reinforcement and intermetallic precipitates. Oxygen reduction is the main driving force behind the corrosion process. Anodization increases pitting resistance of the composites.

INTRODUCTION

Properties such as high strength, low density and reduced coefficient of thermal expansion are the main attributes that have made metal matrix composites (MMC) attractive materials for a range of applications in different industries. A significant amount of data is presently available that relates the processing parameters, microstructure and mechanical properties of MMCs. The corrosion behavior of MMCs has however not been adequately characterized. Among the various MMC systems, the Al alloy - SiC (or alumina) particle combination is considered to be interesting for large scale applications. The composites can be obtained by a number of routes, and of these the liquid metal route is considered to be an economical option.

Published data on the corrosion behavior of Al base MMCs have focussed on aspects related to particle characteristics and processing variables (1-3). Paciej and Agarwala reported about the influence of extrusion ratio and solution heat treatment in powder metallurgically processed AA 7091-SiC composites on overall corrosion resistance (4). The effect of matrix alloy precipitation behavior on pitting susceptibility and the effect of reinforcement on pitting potential and general corrosion susceptibility of powder processed MMCs have also been reported (5,1). The pitting susceptibility of the matrix alloys were not found to alter in the presence of SiC. It has however been shown that changes in the microstructure that take place at the particle/matrix interface effect MMC mechanical properties (6). It is well known that microstructural changes in general influence overall corrosion behavior. This paper presents the effect of matrix composition, particle characteristics such as volume fraction, size and pretreatment as well as composite post treatment such as anodization and the application of ceria coatings on the aqueous corrosion behavior of aluminium alloy base composites.

EXPERIMENTAL

The composites were prepared by the melt stirring route. The procedure consisted of adding preheated SiC or alumina particles to a vigorously stirred molten bath of alloy AlSiMg (Al-7.5Si-1Mg) or AA 2014 (Al-4.5Cu-1Si-0.8Mn-0.5Mg) followed by casting (7). Particle size and content in the composites were varied. The particle pretreatments consisted of (a) preoxidation of SiC at 1100 C in air for two hours, and (b) electroless Ni plating of alumina from a chloride bath for ten minutes followed by rinsing. Table I summarizes the different composites and their characteristics. The microstructures of the various composites were determined following conventional metallographic practices. Details of these studies are not presented here. The composite surface treatments were (a) anodization in 16 wt% sulphuric acid at 23 C and 27 mAcm² for thirty minutes followed by sealing in boiling water for thirty minutes and (b) application of Ce rich coating by prolonged immersion in a cerium nitrate solution. Specimens 10x10x3 mm were cut from the different composites for carrying out the corrosion measurements. These consisted of (a) electrochemical measurements in 3.5% NaCl and (b) 28 days exposure in NaCl. The electrochemical measurements consisted of anodic potentiodynamic polarization from -1400 mV to +100 mV at 10 mV/s in a standard corrosion cell with a SCE reference electrode. Both aerated and deaerated electrolytes were used. Specimens separately exposed at 50 mV above the pitting potential were also examined. After the immersion test the weighed and exposed specimens were cleaned in 50 vol% nitric acid, dried and reweighed.

RESULTS

Electrochemical Measurements

The polarization curves of the different alloys and their composites in both aerated and deaerated NaCl were similar and the pitting potential, denoted by the potential at which the current increases was read from these curves. The corrosion and pitting potentials, E_c and E_p respectively, of the different alloy composites under

Table I - Alloy AlSiMg Composites Designation and Characteristics.

Designation	Reinforcement			
	Type	Volume(%)	size(μm)	Treatment
CA-05-20	Alumina	5	20	-
CA-05-100	Alumina	5	100	-
CA-20-100	Alumina	20	100	-
CNA-05-50	Alumina	5	50	Niplated
CC-05-50	SiC	5	50	-
CC-10-50	SiC	10	50	-
CC-05-100	SiC	5	100	-
CC-10-100	SiC	10	100	-
CC-05-50	SiC	5	50	Oxidized

varying conditions are listed in Tables II e III. In deaerated NaCl E_c of the different specimens were 300-500 mV higher than E_p . The presence of the reinforcement, SiC or alumina, did not affect the potential values of the alloys. These observations differ from data observed elsewhere where SiC addition increased corrosion potential (8).

Table II - Corrosion and pitting potentials of AlSiMg alloy and its Composites in aerated and deaerated 3.5% NaCl (vs SCE).

Specimen	Aerated		Deaerated	
	E_c (mv)	E_p (mv)	E_c (mv)	E_p (mv)
Alloy	-760	-695	-1140	-719
CA-05-20	-736	-608	-1220	-688
CA-05-100	-740	-675	-1240	-625
CA-20-100	-760	-620	-1070	-599
CNA-05-50	-770	-690	- 729	-685
CC-05-50	-735	-639	-1030	-659
CC-10-50	-733	-688	-1130	-678
CC-05-100	-755	-600	- 930	-713
CC-10-100	-744	-721	-1100	-728
COC-05-50	-764	-650	-885	-746

Table III - Corrosion and pitting potential of alloy AlSiMg and AA 2014 composites in As-Cast and Anodized conditions in aerated 3.5% NaCl (vs SCE).

Specimen	E_c (mv)		E_p (mv)	
	As Cast	Anodized	As Cast	Anodized
AlSiMg +CC-05-100	-755	-725	-600	-458
Alloy AA 2014 +CC-05-100	-700	-644	-500	-440

In aerated NaCl the E_c increases and the difference between E_p and E_c reduces to ~100mV. E_c of the alloys in aerated NaCl increases upon addition of the reinforcement. Other particle related parameters did not affect E_c or E_p . Preoxidation of SiC did not alter the potentials, whereas Ni plating of alumina increases E_c of the composites due mainly to the influence of Ni on the potential. The E_c and E_p of AA 2014 in aerated NaCl are higher than those for AlSiMg. This is attributable to the presence of Cu in the former

loy. The E of the anodized specimens were significantly higher than those of the as cast composites, indicating the increased resistance of the anodized specimens to pitting. Similar data were reported elsewhere (1).

Immersion Measurements

The weight change data of various specimens following 28 days exposure to NaCl are shown in Table IV. Weight losses are due to extensive localized and general corrosion of the matrix. The increase in SiC particle content increased corrosion rate, whereas increase in alumina particle content decreased corrosion rate slightly. This behavior can be attributed to the difference in the electrochemical conductivity of the two kinds of particles. Preoxidation of SiC resulted in a slight increase in long term corrosion behavior, due probably to the precipitation of Si on the SiO₂ surface (figure 1). On the other hand, corrosion of the composites with Ni plated alumina increased significantly due to increased galvanic effects.

Table IV - Average Corrosion Weight loss in 3.5% NaCl, pH 7.0 after 28 days.

Specimen	Weight loss (mdd)	Specimen	Weight loss (mdd)
Alloy AlSiMg	5.28		
CC-05-20	2.37	CA-05-20	4.75
CC-05-50	3.41		
CC-05-100	5.6	CA-05-100	4.45
CC-10-50	4.67	CA-10-50	4.61
CC-10-100	6.12	CA-10-100	4.38
COC-05-50	5.28	CNA-05-100	12.05

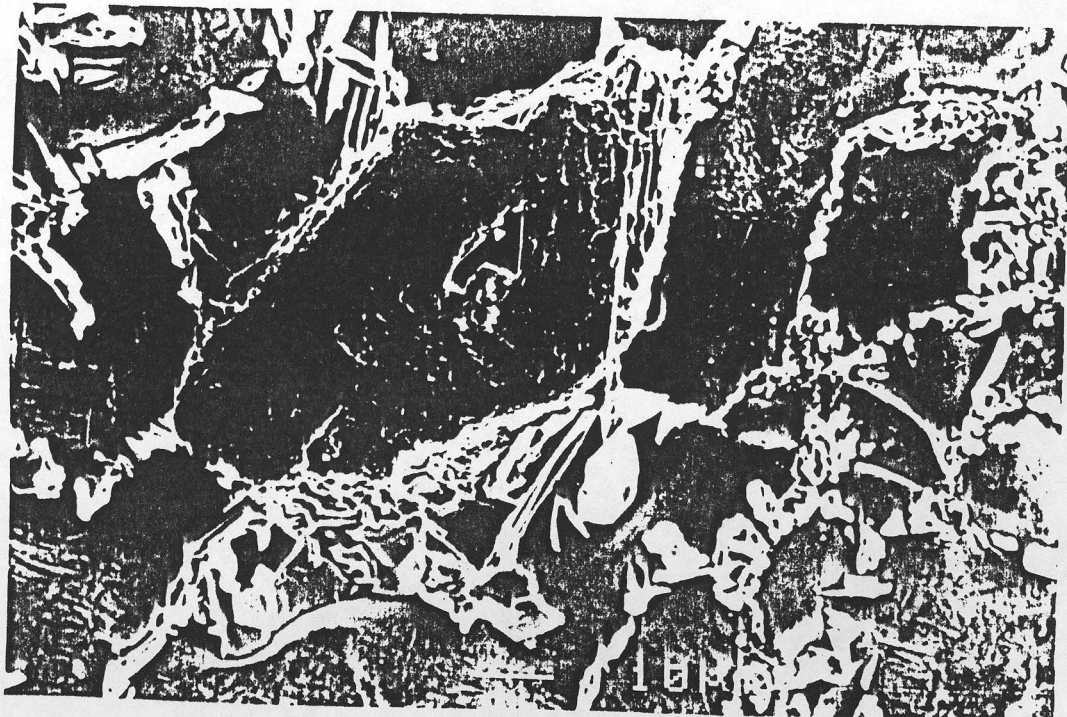


Figure 1 - Scanning electron micrograph of composite COC-05-50 exposed to 3.5% NaCl for 28 days.

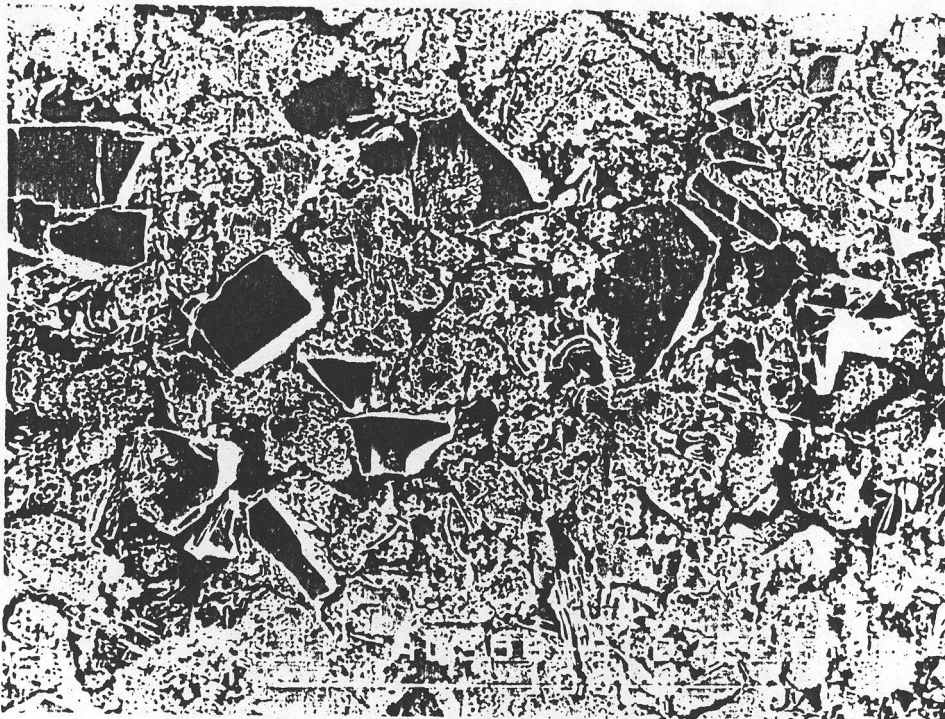


Figure 2 - Scanning electron micrograph of composite CC-05-50 exposed at 50 mV above E_p for 5 minutes.



Figure 3 - Scanning electron micrograph of composite CC-05-50 exposed at 50 mV above E_p for 5 minutes.

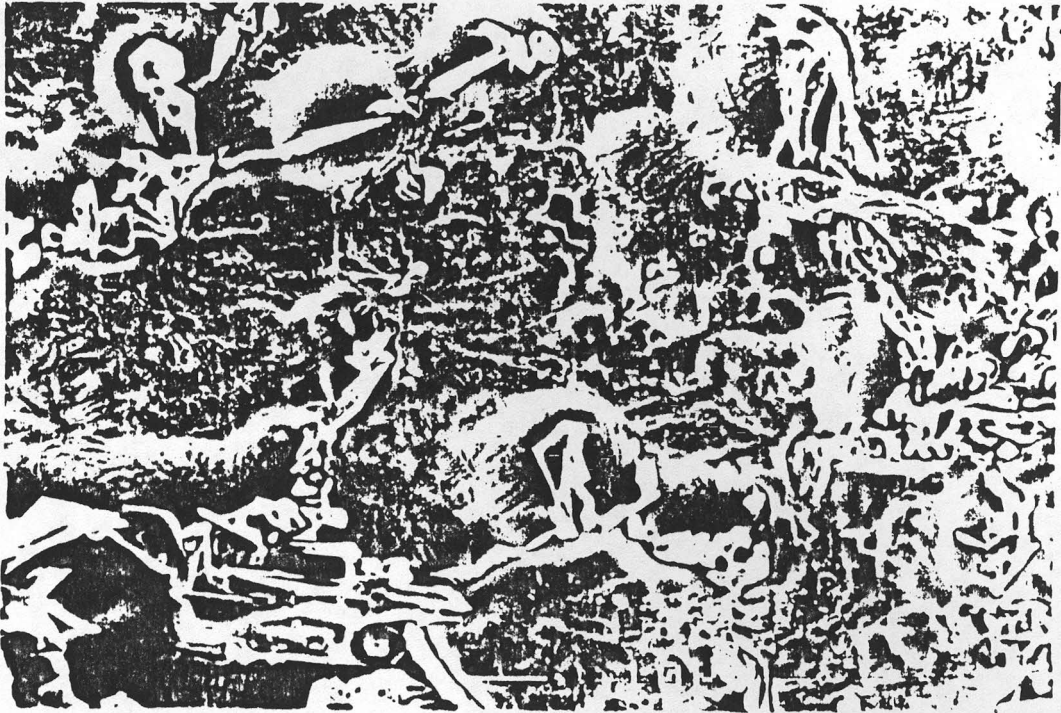


Figure 4 - Scanning electron micrograph of matrix region of composite CC-05-100 exposed to 3.5% NaCl for 28 days.

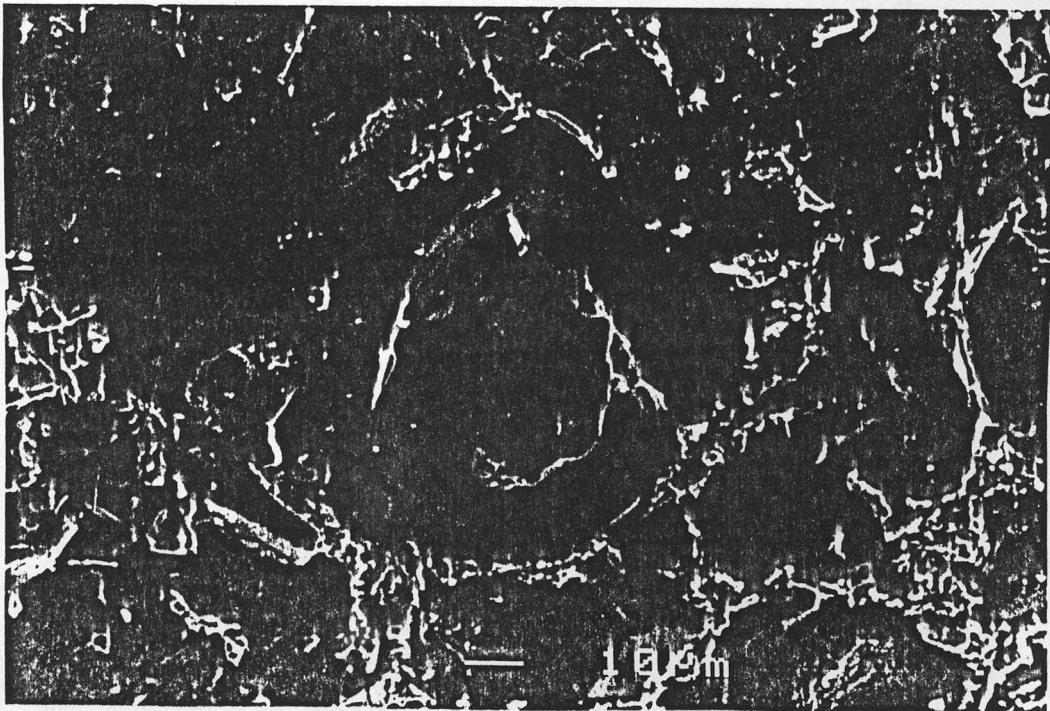


Figure 5 - Scanning electron micrograph of composite CC-05-50 exposed to 3.5% NaCl for 28 days.

The composite specimens exposed at 50 mV above E_p revealed (a) crystallographic pits in the matrix and (b) microcrevices in the vicinity of the reinforcements (figures 2,3). The pits formed in SiC composites were deeper than those formed in alumina composites. Crystallographic facetting has been observed in both the alloy and the composites, contrary to observations made elsewhere (1,9). In most of the specimens exposed for 28 days to NaCl, dimpled regions were observed. (figure 4). In both types of composites (a) particle drop-out was observed as a consequence of matrix dissolution around the reinforcement, and (b) formation of a number of smooth hemispherical pits (figure 5). Overall comparison of the two types of composites with identical volume fraction of particles revealed that after 28 days exposure, more alumina particles were retained in place as compared to the SiC particles. This is attributable to the higher cathodic reactivity of the SiC particles.

GENERAL DISCUSSIONS

The formation of significantly more number of pits in the composites as compared to that in the as cast alloy can be directly linked to the presence of a greater number of heterogeneities. These in the composites are a mixture of the following: casting defects, intermetallic precipitates, the reinforcements and reinforcement/matrix interaction products. The composites as compared to the cast alloy revealed a greater number of intermetallic precipitates. Similar data were reported by Turnbull (10). Consequently, notwithstanding heterogeneities such as the reinforcement and the products the number of candidate sites for pit initiation in composites are higher.

The fact that in quiescent aerated chloride solutions Al alloys and composites pit spontaneously and have corrosion potentials more negative than in deaerated NaCl, the driving force for the corrosion reaction in aerated solutions is the cathodic oxygen reduction reaction. In the unreinforced alloy, precipitates are the cathodic sites, whereas in the composites the cathodic sites are one or a combination of (a) the reinforcement (as in the case of SiC), (b) the precipitates or (c) the interaction products. The formation of crevices can be attributed to changes in the particle/matrix interface composition which in turn is due to specific composite processing conditions.

Summarizing, it can be stated that the introduction of the reinforcement brings about corrosion problems that can be associated to (a) galvanic effects, as in the case of SiC, (b) particle/matrix interaction products (a typical example is the formation of Al_4C_3 , a water soluble reaction product in Al/SiC composites) and (c) particle/matrix interfacial defects which lead to formation of microcrevices and voids.

CONCLUSIONS

1. In aerated NaCl the E_c was 300-500 mV more than in deaerated NaCl. The E_p was however unaffected by aeration.
2. In aerated NaCl the E_p of composites were higher than those of the alloy.
3. Pitting was the major form of corrosion in both the alloy and the composites. The number of sites for pit initiation in the composite were significantly higher and included the reinforcement, the interaction products and the intermetallic precipitates.
4. The oxygen reduction reaction is the major driving force for the corrosion reaction. The SiC and the precipitates were the cathodic sites in the composites.

Pits were crystallographic in nature and those in SiC composites were deeper than those in alumina composites. Prolonged exposure in NaCl resulted in formation of hemispherical pits, due mainly to dissolution effects in the quiescent solution adjacent to the surface.

6. Composite surface treatment such as anodization and cerium coatings increased pitting resistance.

REFERENCES

1. P.P. Trzaskome, E. McCafferty and C.R. Crowe, "Corrosion Behavior of SiC/Al Metal Matrix Composites", Journal of Electrochemical Society, vol. 130, no. 9, 1983, 1804-1809.
2. M. Metzger and S.G. Fishman, "Corrosion of Aluminium Matrix Composites. Status Report", Industrial Engineering, Chemical Products, Research and Development, vol. 22, no. 2, 1983, 296-302.
3. D.M. Aylor and P.J. Moran, "Effect of Reinforcement on the Pitting of Aluminium-Base Metal Matrix Composites", Journal of Electrochemical Society, vol. 32, no. 6, 1985, 1277-1281.
4. R.C. Paciej and V.S. Agarwala, "Influence of Processing Variables on the Corrosion Susceptibility of Metal Matrix Composites", Corrosion, vol. 44, no. 10, 1988, 680-684.
5. J.F. McIntyre, R.K. Conrad and S.L. Golledge, "The Effect of Heat Treatment on the Pitting Behavior of SiC /AA2124", Corrosion, vol. 46, no. 11, 1990, 902-905.
6. D.J. Lloyd, H.P. Lagace, and A.D. Mcleod, "Interfacial Phenomena in Metal Matrix Composites", in "Controlled Interphases in Composite Materials", ICCI-III, Editor. H. Ishida, Elsevier, 1990, 359-376.
7. L.V. Ramanathan and P.C.R. Nunes, "Effect of Liquid Metal Processing Parameters on Microstructure and Properties of Alumina Reinforced Al Base MMC", Metal Matrix Composites - Processing, Microstructure and Properties - 12th Risø International Symposium, Eds: N. Hansen et. al. Risø, Denmark, 1991, 611-616.
8. E. Maahn and S. Roepstorff, "Corrosion Resistance of Aluminium-Silicon Carbide Materials", Metal Matrix Composites - Processing, Microstructure and Properties, 12th Risø International Symposium, Eds. N. Hansen et. al., Risø, Denmark, 1991, 497-502.
9. P.P. Trzaskoma, "Pit Morphology of Aluminium Alloy and Silicon Carbide/Aluminium Alloy Metal Matrix Composites", Corrosion, vol. 46, no. 5, 1990, 402-409.
10. A. Turnbull, "Review of Corrosion Studies on Aluminium Metal Matrix Composites", British Corrosion Journal, vol. 27, no. 1, 1992, 27-35.