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EFFECT OF REINFORCEMENT CHARACTERISTICS ON THE CORROSION OF PARTICULATE REINFORCED ALUMINIUM COMPOSITES

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Abstract

Silicon carbide (or alumina) particle reinforced aluminium alloy base composites are being considered for a wide range of applications. Their mechanical properties have been investigated in detail, but only limited information is available about their corrosion behavior. This paper presents the influence of particle related parameters such as composition (SiC, alumina), size (10-100 μm), volume fraction (5-20%) and pretreatment (preoxidation, nickel plating) on the corrosion behavior of AlSiMg alloy matrix composites in 3.5% NaCl solutions. Prolonged immersion tests and anodic polarization measurements have been carried out. All the composite specimens pitted and the particle/matrix interfacial regions were the preferred sites for pit initiation. The SiC particles and precipitated second phases were the cathodic sites for oxygen reduction in the SiC and alumina composites respectively. The pitting potential 'E_p' varied with the addition of the reinforcement and the open circuit corrosion potential 'E_{corr}' was dependent on the extent of aeration. The formation of crystallographic pits and microcrevices were observed on a number of specimens. The extent of pitting attack decreased in composites reinforced with preoxidized SiC particles. The overall mechanism of pit initiation and propagation has also been discussed.

Keywords

Metal matrix composites, aluminium, reinforcement, silicon carbide, alumina, corrosion.

Introduction

A combination of properties such as high strength and stiffness, low density and reduced coefficient of thermal expansion have made metal matrix composites (MMC) attractive materials for a range of applications which include defence, aerospace, automotive and sports equipment. Presently, a significant amount of data is available about the mechanical properties and correlations between processing route, microstructure and properties of MMCs. However only limited information is available about its environmental stability or corrosion behavior. This aspect is closely associated with the presence of heterogeneities, and MMCs have a large quantity of heterogeneities in the form of the reinforcement, microcrevices, voids, porosity as well as other precipitates. Although MMCs encompass a very wide range of matrix/reinforcement combinations, the aluminium alloy/SiC (or alumina) particle combination seems to be one of the most interesting for industrial applications. These composites can be produced by a variety of techniques and although the powder metallurgy route has been used quite extensively, the molten metal route is considered to be cost effective for large scale production.

A few corrosion studies on SiC/Al base alloy MMCs have focussed on the effects of reinforcement material on pitting potential, pit morphology and general corrosion susceptibility in chloride solutions (1-3). Trzaskoma et.al. observed that the pitting susceptibility of a number of common matrix alloys did not alter upon addition of SiC (1).They also found the MMCs to be less resistant to pit initiation.Paciej and Agarwala investigating the effects of processing variables, found that a high extrusion ratio and modified solution heat treatment enhanced the corrosion resistance of alloy 7091/SiC composites (4). McIntyre et. al reported that the precipitation behavior of heat treatable matrix alloys to alter the pitting susceptibility in the presence of SiC (5). It has also been shown that changes taking place at the matrix/reinforcement interface affect mechanical behavior of MMCs (6). These changes are due to a combination of one or more of the following: matrix alloy, particle surface characteristics, processing route and subsequent heat treatment. The interfacial changes are usually in the form of variations in local composition, formation of precipitates, or other reaction products, and these affect corrosion behavior. In order to characterize this aspect, an investigation was undertaken to verify the effects of particle composition, volume fraction, processing route, matrix alloy, particle pretreatment and MMC heat and surface treatment on the aqueous corrosion behavior. This paper presents the effect of reinforcement pretreatments on the corrosion behavior AlSiMg alloy/SiC (or alumina) composites.

Experimental

Materials

An Al-7.5%Si-1%Mg alloy was used for preparing the MMCs. The composites preparation procedure consisted of adding preheated (and where relevant, pretreated) particles of either SiC or alumina to a vigorously stirred molten bath of the alloy. After 10 minutes agitation, the composite was poured into chilled copper molds and allowed to solidify. Particles of varying sizes were used and composites with different particle volume fraction were prepared. The particle pretreatments consisted of (a) preoxidation of the SiC particles at 1100 C in air for 2 hours, (b) electroless nickel plating of the SiC and alumina particles from a chloride bath for 10 minutes followed by rinsing and (c) preheating of the particles with sodium tetraborate at 300 C for 2 hours. The composite processing parameters such as melt temperature, stirrer design, stirring rate and duration etc. which affect reinforcement distribution were maintained at their optimized values to obtain uniform particle distribution (7). Specimens 10x10x3mm were cut from the prepared composites for corrosion measurements.

Corrosion measurements

The corrosion measurements consisted of (a) long term immersion tests in 3.5% NaCl at 25 C for 28 days and (b) anodic polarization in 3.5% NaCl. Specimens of the various composites listed in Table I were prepared for the long term tests by grinding to 600 grit, degreasing and rinsing. The weighed specimens were suspended within a temperature controlled bath of NaCl. The pH was maintained constant at 7. After the test, the specimens were cleaned in 50vol% HNO_3, dried and weighed. The specimens for the electrochemical measurements were cut to size 5x5x3mm, cold mounted in epoxy resin, ground to 600 grit, rinsed and introduced into a standard corrosion cell. The specimens were allowed to equilibrate prior to measurement of the open circuit corrosion potential and initiation of anodic potentiodynamic polarisation scans from -1400mV to +100mV at 10mV/s. The potential vs current curves were recorded. Measurements were carried out in both aerated and deaerated NaCl solutions.Deareation was achieved by bubbling nitrogen through the electrolyte before and during the measurements.In tests carried out to verify the effect of reinforcement on pit morphology, one half of the exposed surface of the specimen was masked with a lacquer prior to exposure in th electrolyte at 50mV above its pitting potential for 15 minutes. These specimens were then rinsed, dried and examined in a SEM/EDAX.

Results and Discussions

Microstructural aspects

The as cast microstructures of alloy AlSiMg and the composites containing SiC and alumina are shown in figure 1. The structure of the alloy and the matrix in the composite consist of primary dendrites and silicon particles. The reinforcement can be observed to be well distributed. Significant improvements in particle distribution were achieved by controlling the composite processing parameters. Nevertheless, particle clustering could not be completely eliminated.

Electrochemical measurements

The anodic polarization curves of alloy AlSiMg and the composites in aerated and deaerated NaCl solutions were found to be similar and Figure 2 shows typical curves for AlSiMg' in aerated and deaerated NaCl. The pitting potential E_p, denoted by the potential at which the current increases was read from these curves. Table II lists E_p and E_{corr} of the different specimens. It can be seen that in deaerated NaCl, E_p of the alloy and composites is 300 to 500mV higher than E_{corr}.In the latter, it was independent of the composition of the reinforcement. On the other hand, in aerated NaCl, the difference between E_p and E_{corr} is ~100mV. The E_{corr} of the alloy and the composites are higher in the aerated solution as compared to that in the deaerated solution. The E_p of the alloy and the composite although lower in the aerated solution varied only by ~100mV. The addition of the reinforcement did not alter the E_{corr} of the alloy in the aerated NaCl, but increased (with the addition of SiC) in the deaerated NaCl. Maahn and Roepstorff also reported similar increase in E_{corr} with SiC addition and further increase in E_{corr} with increasing SiC content (8). The E_p of the composite with SiC is higher than that of the alloy. Similar observations were reported elsewhere (1).

Long term immersion tests

Weight loss data for the alloy and the composite specimens following 28 days immersion in 3.5 NaCl are given in Table III. It can be observed that the extent of corrosion was considerable in all cases. The corrosion rate of the unreinforced alloy although high, decreased slightly when 5vol% of 100 μm alumina particles were added. Increase in the particle content resulted in increase in weight loss. The addition of 5% of SiC did not alter significantly the extent of corrosion of the alloy. On the other hand, the corrosion rate of the composite containing 20% of 10 μm SiC was appreciably lower than that of the alloy. The weight losses observed in all the specimens after prolonged exposure to NaCl were provoked by pitting of the matrix.

Pit morphology

Two sets of pit morphological studies were carried out. In the first, specimens held for 15 minutes at 50mV above E_p in NaCl were examined. In the second, the specimens exposed to 3.5% NaCl for 28 days were examined. In alloy AiMgSi exposed at a fixed potential, a number of pit clusters were observed as shown in figure 3a. At higher magnifications, the attacked regions were found to be in the vicinity of the elongated Si particles. In the alumina containing composites, microcrevice formation was observed at the interfacial regions and in their vicinity (figure 3b). In many respects, the nature of the attack was similar to that observed in the alloy. The cathodic regions in the alumina composites were probably the precipitated second phase particles. The microcrevice formation was more widespread in composites with reduced alumina particle size. Corrosion products were also observed near the crevices as shown in figure 3c. At higher magnifications, crystallographic facetting was observed (figure 3d). In specimens where a portion of the surface was masked prior to polarization in NaCl, a region close to the masked/unmasked boundary also revealed typical crevicing at particle clusters as shown in figure 3e. The pits formed in SiC composites were deeper (figure 3f) than those formed in alumina composites (figure 3e). formed under identical conditions. Trzaskoma et.al. reported the formation of shallow pits in SiC/6061 composites as compared to those in the unreinforced alloy (1,9). In this investigation, it has been observed that in SiC composites, the pit sizes varied considerably from 5 to 20 μm where as in the parent alloy and in the alumina composites the "trenches" were 50 to 150 μm long and 2-20μm wide. Crystallographic facetting has been observed in both the alloy and in the composites contrary to observations reported elsewhere (10).

In the as cast alloy exposed for 28 days, the pits even though few, were deeper as shown in figure 4a. The pits were crystallographic, with no evidence of facetting. The lack of facetting could be attributed to the prolonged exposure during which preferential dissolution of the edges may have taken place. In almost all the cases, in the initial stages, the interdendritic or intergranular Si was unaffected, leading eventually to their dropping out. At higher magnifications, the intergranular regions were found to be smooth and shallow (figure 4b). In the alumina composites also, preferential dissolution of the matrix lead to particle dropout (figure 4c&d). In the latter,smooth hemispherical pits formed around the particles.The extent to which interfacial regions were attacked is higher in SiC composites as compared to that in alumina composites. After 28 days exposure, more alumina particles were in place as compared to SiC particles in the respective composites. This behavior could be attributed to the higher cathodic reactivity of the SiC particles and also to the higher NaCl concentration in this investigation as compared to that used elsewhere (1).

General Discussions

In chloride ion containing solutions aluminium alloys generally pit. This has been observed, both in the unreinforced alloy as well as in the matrix of the composite. Pits usually initiate at surface heterogeneities and these in the cast alloy or the composite matrix are one or a combination of the following: (a) Casting defects. These usually occur as a result of solidification shrinkage and hydrogen liberation; (b) Second phase particles or precipitates such as Mg_2Si. These form when cast Al alloys are heat treated to achieve an optimum combination of strength and ductility, (c) Reinforcements and (d) Reinforcement/matrix interaction products. In this investigation, Mg_2Si particles were observed in the matrix surrounding the SiC particles. Additionally the total number of intermetallic precipitates in the matrix were found to be considerably higher in the composite than in the unreinforced alloy subjected to identical treatments. Similar observations were reported by Trzaskoma (9). Consequently, candidate sites for pit initiation in the composites were significantly higher. In the unreinforced alloy, the intermetallic particles were the cathodic sites, whereas in the composites, depending on the composition of the reinforcement, the second phase particles or the interfacial reaction products were the cathodic sites for the oxygen reduction reaction.

Particle pretreatment effects

The composites containing oxidized SiC particles revealed fewer pits and these too were significantly smaller than the pits found in composites containing unoxidized SiC. Reduced pit size could be attributed to (a) reduced reaction between the particle and the matrix above the liquidus and (b) reduced cathodic efficiency of the oxidized SiC. It is widely known that in Al base composites at temperatures above the liquidus, the Al reacts with SiC to form Al_4C_3. Although this reaction is stifled if the Si content of the alloy is high, it has been shown that in A356 with 7.5% Si, Al_4C_3 does form according to reaction 1.(6).

$$4Al + 3SiC \longrightarrow Al_4C_3 + 3Si \qquad (1)$$

Al_4C_3 is soluble in water and thereby decreases the corrosion resistance of the composite. The increase in the Si as a result of reaction 1 also affects the corrosion behavior of the composite in so far as increasing the number of cathodic sites. Oxidation of the SiC particles results in a 50 A thick layer of SiO_2 on the particle, and this stiffles the above reaction. Even though SiO_2 has been reported to react with the matrix according to reactions 2 and 3, the former takes place when the SiO_2 layer is thin, (5 A) and both (the reactions), when the oxide layer is thicker (11).

$$2Al + Mg + 2SiO_2 \longrightarrow MgAl_2O_4 + 2Si \qquad (2)$$

$$2Mg + SiO_2 \longrightarrow 2MgO + Si \qquad (3)$$

Consequently, the kinetics of the particle/matrix interfacial reaction are reduced and the interfacial products formed thereof are considerably thinner and less detrimental than those formed on composites with unoxidized SiC particles.

The extent of pitting of composites reinforced with Ni plated SiC was significantly more than those reinforced with as received SiC. This increased pitting behavior is attributable to the more noble Ni on the SiC behaving as efficient cathodic sites for oxygen reduction.

Mechanism

The fact that (a) in quiescent aerated chloride ion containing solutions, unreinforced and reinforced Al alloys pit spontaneously and (b) in aerated NaCl the corrosion potential of the Al alloys is more negative than in deaerated NaCl, the primary driving force in aerated media is the cathodic reduction of oxygen. In the unreinforced alloy, due to the poor conductivity of the oxide film, the oxygen reduction reaction is confined to localized areas of the surface associated with impurities or precipitate particles.Hence,when unreinforced alloy specimens are exposed to aerated NaCl,they reveal only a few deep pits.The introduction of ceramic reinforcements increase the density of heterogeneities, which in turn affect the electrochemical and corrosion behavior of the alloy. Since SiC is noble to the matrix in NaCl, they act as the net cathodic sites. It has also been shown by surface analysis that the surface density of intermetallic particles is a factor of two greater for the reinforced alloy as compared to a similarly processed monolithic alloy (10). Consequently, in (a) alumina reinforced composites, the increased number of pits are due primarily to the weak spots in the oxide film covering these intermetallic particles and (b) in SiC composites, the cathodic current density is lower by an order of two (since it is distributed over many spots) and therefore results in shallow pits.The increased number of pits in the SiC composites could also be attributed to more numerous SiC/Al interfaces,(which are preferred sites for film breakdown),as compared to the "preferred" sites in unreinforced alloy. The pitting behavior of composites in aerated solutions is controlled by oxygen depolarization and this varies linearly with the cathode to anode area ratio. In situations, where clustering of particles takes place, the local cathode to anode ratio is altered and therefore the pitting behavior.

Specific composite processing cnditions have also resulted in alteration of the particle/matrix interface composition and henceforth in the formation of crevices rather than pits. Similar data were reported by Aylor and Moran for $SiC_w/6061$ (PM) composites (3).

Overall, it can be stated that the introduction of the reinforcement into the matrix alloy gives rise to 3 kinds of corrosion problems: (a) those associated with galvanic effects.In SiC composites, the particles are more noble. In alumina composites, galvanic coupling exists to a reduced extent between the precipitated second phases and the matrix; (b) those associated with particle/matrix reaction products.These products are generally intermetallic precipitates and the oxide on the composite surface covering these precipitates are the preferred or weak spots for pit initiation; (c) formation of microcrevices at the interfaces and voids. Certain interfacial defects arise from incomplete cohesion between reinforcement and matrix.In these defects local chemistry necessary to retard local repassivation is easily achieved and results in formation of crevices or trenches. In this investigation, all 3 forms of defects induced by particle addition have been observed,either singly or jointly. A significant reduction in the number of pits formed, at least to the extent of SiC not acting as the net cathode or as a consequence of interfacial reaction products has been observed when high temperature preoxidized SiC particles are used. A further step towards reducing the pitting behavior in composites could be achieved by application of conversion coatings and/or reactive element impregnated coatings. This investigation is being extended to include studies related to application of these coatings and their effects on composite corrosion behavior.

Conclusions

1. In NaCl solutions the corrosion potential of the alloy and the composites increased in the presence of dissolved oxygen.

2 The pitting potential `E_p' of the alloy and the composite were not affected significantly by aeration of the solution.

3. E_p of the composites were higher than that of the alloy in aerated NaCl.

4 The particle/matrix interfacial regions were the preferred sites for pitting.

5 In the presence of the reinforcement, a significant increase in the number of precipitated second phases in the matrix was observed.

6 The SiC particles and the precipitated phases were the sites for cathodic oxygen reduction in the SiC and alumina composties respectively.

7 The pits were crystallographic in nature and those in SiC composites were shallower than those formed in the alumina composites.

8 Microcrevice formation was also observed,due possibly to particle/matrix decohesion.

9 Composites containing preoxidized SiC particles pitted less than those with as received SiC particles.

10 Particle addition gives rise to three kinds of corrosion related problems: galvanic effects; particle/matrix reaction product induced effects; and interfacial microcrevicing.

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Figure 1. Optical micrographs of as cast (a) AlSiMg alloy, (b) alumina composite and (c) SiC composite.

Figure 2. Anodic potentiodynamic polarization curves of alloy AlSiMg in 5% NaCl. (a) aerated (b) deaerated.

Figure 3. Scanning electron micrographs of (a) alloy AlSiMg, (b),(c),(d),(e) alumina composite and (f) SiC composite surfaces exposed for 15 minutes at 50mV above E_p in 3.5% NaCl.

Figure 4. Scanning electron micrographs of (a) (b) AlSiMg alloy, (b) alumina composite and (c) SiC composite exposed to 3.5% NaCl for 28 days.