

## EFFECT OF AGING ON CORROSION BEHAVIOR OF SiC<sub>p</sub> - AL COMPOSITES

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### ABSTRACT

*This paper describes the influence of aging A356, AA6063, AA2014 and their SiC particle reinforced composites ( 10 vol % ) prepared by the melt stirring process on their aqueous corrosion behavior. Electrochemical measurements and immersion tests in 3.5 % NaCl were carried out. The Brinell hardness of AA2014 / SiC and A356 / SiC composites were lower than those of the corresponding monolithic alloys aged to the same extent. The composites corroded at a higher rate than the alloys. The corrosion rates of the composites increased with aging times and the SiC / matrix regions with the higher concentration of precipitates were the preferred pitting sites and this lead to SiC particle drop out.*

Key words: Composites, aging, corrosion.

### INTRODUCTION

Presently a significant amount of data is available about the mechanical properties and correlations between processing route, microstructure and properties of MMCs. More information concerning their corrosion behavior is needed. This aspect is closely related to the presence of heterogeneities, and MMCs have a large quantity of heterogeneities in the form of reinforcement, microcrevices, voids, porosity, intermetallic precipitates and interaction products. The aluminium alloy / SiC 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.

Corrosion studies carried out on Al alloy / SiC composites in NaCl have shown localized corrosion to take place and to be controlled by alloy and reinforcement related parameters.[1-5]. The precipitation kinetics in composites of age hardenable Al alloys are different from that in the unreinforced matrix alloy [6]. Also, changes taking place at the matrix / reinforcement interface affect mechanical behavior of MMCs [7]. This paper describes the effects of matrix alloy composition and aging on the corrosion behavior of Al / SiC composites.

### MATERIALS AND METHODS

Alloys A356 ( Al-7.5Si-0.5Mg ), AA2014 ( Al-4.5Cu-1Si-0.8Mn-0.5Mg ) and AA6063 ( Al-0.5Si-0.8Mg ) were used to prepare the composites containing 10 vol% of SiC ( average size of 50  $\mu$ m). The composites were prepared by the melt stirring process and the methods of preparation have been previously reported.[8]. Alloy and composite specimens were solubilized at 500°C for 1.5 h followed by quenching in water and then aged at 190°C for 2-14 h. Age hardness of the various specimens was evaluated using Brinell macrohardness measurements. Microhardness measurements were not carried out as they were prone to be erroneous due to the possibility of making indentations in the matrix just above the SiC particle.

The corrosion measurements consisted of (a) anodic potentiodynamic polarization in 3.5% NaCl and (b) immersion tests in 3.5%NaCl at 25°C for 28 days. Specimens for the electrochemical measurements were cut to size (5x5x3mm), mounted in epoxy,ground to 600 grit,rinsed and introduced into a standard corrosion cell. The specimens were allowed to equilibrate prior to measurement of their corrosion potential  $E_{corr}$  and initiation of anodic 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. The immersion test specimens ( 10x10x3mm) were suspended in 3.5%NaCl maintained at 25°C and pH 7. After the test the specimens were cleaned in 50 vol% nitric acid, dried and weighed. In tests carried out to study pit morphology, specimens were exposed to 3.5% NaCl at various potentials close to  $E_p$  for different durations. The specimens were rinsed and examined in a scanning electron microscope with analytical attachments.

### RESULTS AND DISCUSSION

**Microstructure and hardness** The as cast microstructures of alloy A356 and its composites revealed primary dendrites, eutectic silicon and the reinforcement. Alloy AA2014 revealed intergranular CuAl<sub>2</sub> distributed throughout and alloy AA6063 a fine distribution of nearly rounded Mg<sub>2</sub>Si. The microstructures of the composites revealed besides the

Table 1. Brinell hardness of the alloys and composites in as solubilized state and aged at 190 C

Aging time hours	Brinell Hardness					
	AA2014		A356		AA6063	
	Alloy	Composite	Alloy	Composite	Alloy	Composite
Solubilized	81.3	69.0	61.0	51.0	35.3	43.2
2	122.8	116.6	91.2	85.4	44.1	66.1
4	126.8	111.2	96.6	95.4	60.2	60.0
6	130.4	124.0	89.0	87.0	58.6	62.2
8	125.2	117.0	91.0	89.2	57.4	58.0
10	133.0	125.8	90.0	90.2	60.2	59.6
12	118.0	121.6	83.8	69.3	55.5	64.0
14	123.0	107.0	83.6	88.0	62.0	60.3

Table 2. Corrosion and pitting potentials of the alloy and composite specimens in aerated 3.5%NaCl at 25°C (vs SCE)

Alloy/Composite	$E_{corr}$ (mV)	$E_p$ (mV)
A356	-760	-620
A356/SiC	-759	-600
AA2014	-690	-575
AA2014/SiC	-700	-590
AA6063	-730	-700
AA6063/SiC	-723	-690

Table 3. Corrosion weight loss of the aged alloys and composites.

Aging time hours	Corrosion weight loss ( mdd)*					
	A356		AA2014		AA6063	
	alloy	composite	alloy	composite	alloy	composite
2	4.41	4.72	6.10	6.51	1.08	4.20
4	4.71	4.97	6.59	6.32	1.13	3.93
6	4.86	5.48	5.92	6.71	2.44	11.2
8	5.01	4.81	6.91	6.91	3.76	11.13
10	5.28	4.37	5.78	6.32	3.82	11.39
12	5.17	5.77	5.90	7.08	4.04	13.29
14	4.72	6.26	6.16	7.32	4.01	10.66

\*mdd - milligrams per square decimetre per day

above mentioned features for the different alloys, also a fair distribution of SiC particles.

The Brinell hardness of the alloys and composite specimens in the solubilized as well as aged conditions are shown in Table 1. In general the hardness of the

alloys and the composites increased with aging times. The hardness of AA2014/SiC and A356/SiC composites were lower than those of the corresponding alloys aged to the same extent. This is probably due to the regions in the composite specimens where hardness

Measurements were made having a significantly lower concentration of intermetallic precipitates, as compared to that in the alloy. It is well known that intermetallic precipitates form during aging at dislocations, voids and grain boundaries [9,10] In composites, because of the differences in the coefficient of thermal expansion between the matrix alloy and the reinforcement, the regions of the matrix close to the particles have a high density of dislocations and are therefore the preferred sites for intermetallic precipitate nucleation upon aging. The hardness of AA6063/SiC composites on the other hand did not differ significantly from that of the alloy. This could be attributed to the lower alloying element content of this alloy as compared to that of the other two alloys.

## CORROSION BEHAVIOR

The anodic polarization curves of the alloys and their composites were found to be similar in deaerated NaCl.  $E_p$  of the alloy and composites were 300-500mV higher than their corresponding  $E_{corr}$ . Upon aeration of the electrolyte, the difference between  $E_p$  and  $E_{corr}$  reduced to 100mV, due mainly to increase of  $E_{corr}$  [1,4]. Table 2 lists the  $E_{corr}$  and  $E_p$  of the three alloys and their composites. The  $E_{corr}$  of AA2014 and its composite are higher than those of alloy A356, alloy AA6063 and their composites. This is due to the presence of Cu in AA2014 [11]. The addition of SiC particles did not alter significantly the  $E_{corr}$  in deaerated NaCl. These observations differ from those reported elsewhere [12,13] wherein upon addition of SiC, the corrosion potentials became more active.

**Immersion Test Results** In general the weight loss of the composites were higher than those of the corresponding alloys. This increased corrosion weight loss is due to increased corrosion of the composite, and also SiC particle dropout. The overall corrosion rate of the alloys and the composites increased with aging times. McIntyre et.al. reported similar increase in corrosion rate with aging of alloy AA2014 and its composite [14]. In this alloy as in other age hardenable alloys, during aging, intermetallic precipitates formed and these precipitates increase in size with aging times. Since  $CuAl_2$  is electrochemically cathodic to the matrix, they lead to accelerated corrosion of the nearby matrix. Similarly, in the other alloys, eutectic Si, or other reaction products act as the cathodic sites and  $Mg_2Si$  acts as a cathode / anode depending on the composition of the surrounding matrix. In aged SiC particle containing composites, the intermetallics precipitate preferentially near the reinforcement and cause localized corrosion around the particles leading often to particle dropout. It has been reported elsewhere that in AA6063 / SiC composites the aging kinetics increases with particle addition whereas in A356 / SiC composites the aging kinetics are ambiguous with particle addition [15,16]. In this investigation similar trends were observed upon comparison of the corrosion weight loss of the alloys and

the composites. Even though no significant increase in hardness was observed upon particle addition to AA6063, the composites of this alloy revealed a marked increase in the corrosion weight loss compared to the monolithic alloy. This could be attributed to particle dropout as explained earlier. The results of parallel experiments revealed that the percent weight loss due to particle dropout varied from 20-40% depending on many factors which include alloy grain size, particle content of the composite, particle distribution and size and precipitation of intermetallics in the alloy. A more detailed investigation to correlate the above mentioned factors to particle dropout and consequently on overall corrosion weight loss is in progress.

**Pit morphology** Alloy and composite specimens exposed at a fixed potential revealed both sporadic pits and pit clusters. At high magnifications, crystallographic faceting was observed. The pits were deep, contrary to observations made by Trzaskoma et. al.[1,17]. In the as cast A356 and AA6063 alloys exposed to NaCl for 28 days, the pits even though few, were deep and crystallographic where inclusions were present. The matrix close to the eutectic Si, close to the grain boundaries were smooth and dimpled. In AA2014 the corrosion initiated in the matrix adjacent to the more noble  $CuAl_2$ . In the composites, corrosion was predominantly around SiC particles, leading often to particle dropout ..

## GENERAL DISCUSSIONS

In chloride ion containing solutions, Al alloys and their composites generally pit. These pits initiate at surface oxide flaws which correspond to heterogeneities on the metallic surface. In the cast alloy or composite, these heterogeneities include (a) casting defects, (b) the reinforcement, (c) SiC / matrix reaction products and (d) intermetallic precipitates formed during aging. The amount of intermetallic precipitates in the composites are significantly higher than in the unreinforced alloy subjected to similar treatments. Consequently, candidate sites for pit nucleation in the composites are higher. The main driving force for the corrosion process is the cathodic oxygen reduction reaction. The cathodic sites are the eutectic Si and interaction products in the Si containing alloys, and  $CuAl_2$  in AA2014. In the composites, besides the above mentioned constituents the SiC particles and the particle matrix reaction products also act as the cathodic sites. The  $Mg_2Si$  precipitates being more active are also prone dissolution. Pit nucleation involves  $Cl^-$  absorption at the flaws in the surface oxide film followed by chemical reaction [18]. During pit propagation the role of the heterogeneities in the alloy / composite control the process. The presence of a very large number of intermetallic precipitates such as  $CuAl_2$  or  $Mg_2Si$  due to aging and the mostly more noble eutectic Si and SiC in the composites leads to extensive pitting of the matrix in the composite. Also

since a significant amount of the precipitates are formed close to the reinforcement, the matrix around the SiC dissolve and lead to particle dropout. Increase in aging time leads to increase in number of precipitates and consequently increased corrosion. The differences in the corrosion rates of the composites of the different alloys aged to the same extent are due to differences in the electrochemical properties of the precipitates and their location.

## CONCLUSIONS

1. The Brinell hardness of the composites AA2014 / SiC and A356 / SiC were lower than those of the corresponding monolithic alloys aged to the same extent, indicating preferential precipitation of intermetallics near the interfacial regions in the composites.
2. The hardness of alloy AA6063 and composite AA6063 / SiC did not vary much as compared to the other alloys, due probably to the lower alloying element content of this alloy.
3. The hardness of the alloys and the composites increased upon aging upto 10h and thereafter decreased.
4. In NaCl solutions, the pitting potential of the alloys and the composites were not affected by aeration of the solution.  $E_p$  of the composites were higher than those of the alloys.
5. Pit initiation sites in the composites were higher than in the alloys. The particle / matrix and precipitate / matrix regions were preferred sites for pitting and dissolution.
6. The oxygen reduction reaction is the driving force for the corrosion process and SiC particles, eutectic Si and precipitated phases are the cathodic sites.
7. The pits were crystallographic in nature and preferential pitting around SiC particles lead to particle dropout.

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