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SEM Observations On The Porosity Activities During Corrosion Of Al- Si-Mg/SiC$_p$ Metal Matrix Composites

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ABSTRACT

The corrosion mechanisms of the clusters and gas porosities in Al–Si–Mg based metal matrix composites(MMCs) reinforced with SiC particles were determined by SEM observations in deaerated 3.5 wt.% NaCl aqueous solutions. It was found that the composites shown severe pitting behaviors which could be due to the presence of aggressive Cl^{-1} ions in the solution. In addition, SEM observations revealed that corrosion preferentially started around of cluster and gas porosities and these observations were correlated with the dissolution mechanisms of aluminium.

KEYWORDS

Cluster;
Porosity;
Corrosion;
SiC particle;
MMC.

INTRODUCTION

Al-Si-Mg alloys are commonly used in the automotive industry, especially for cylinder blocks, piston inert rings, valve filters. The principal reasons for the usage of Al-Si-Mg alloys are their high wear resistance, low density, good corrosion resistance and improved elevated temperature properties[1-3]. Aluminum based metal matrix composites(AMMCs) reinforced with ceramic particulates are the most common and the cheapest materials using for engineering applications principally in the defensive and aerospace industries[4-5].

Porosities are one of the most important of main obstacles to the production of stir-casting composites[6-8]. It is well known that the presence of porosities in the final structure has a negative effect on the usability of the MMCs because they cause a significant reduction in the mechanical properties such as fracture or fatigue strength of the composites[9]. In generally, fatigue behavior of the composite is related to crack initiation and growth mechanisms[10]. The porosities act as fracture starting points in the cast microstructure. Moreover, there are heterogenous stress distributions around the porosities. These porosities may have formed mainly in two ways: (a) due to the aggregation of the pushed reinforcement particles by the matrix dendrites during solidification which is called ‘clusters’, (b) due to the diffusion of hydrogen gas in to the molten metal which is called ‘gas voids’[6, 11-12]. According to Throwsdale et al.[13], a significant contribution to the increased pitting susceptibility arises from the presence of voids and crevices at the reinforcement/matrix interface and relatively large voids created by stretch could act as fine crevices, thus altering the normal pitting behaviour of the composites. It is well known that during the fabrication of particle reinforced MMCs, reinforcements may crack or break into pieces and in the case of the potential of composite exceed E_{pit}, pitting may form and grow at these cracks[12-14]. In addition, areas which have different potentials may increase and when the potential exceed E_{corr} value, these areas may act as pit nucleation sites[15-16]. Similar results were also obtained in our previous studies[14, 17] and were in agreement with depictions observed by Turnbull[18].

The determination of the corrosion behaviour of composites is based on the knowledge of the relationship between the microstructure and its macroscopic response. This can be achieved by the determination of the corrosion phenomenon of the porosities. However, only a few investigations about the porosity effect on the corrosion behavior of aluminium MMCs have been reported. Therefore, preliminary results on the activity of the porosities during the corrosion tests of Al-Si-Mg/SiC_p composites are reported in this study.

EXPERIMENTAL

Al-Si-Mg alloy was used as the matrix alloy with the following composition in wt%: 7.0Si, 0.7Mg, balance Al. The matrix alloy was reinforced with 10 and 20% vol. of SiC particles by using the stir-casting technique. Firstly, in order to prevent the formation of Al_4C_3, the surface of SiC particles were oxidized at 900°C before added into the semi-solid matrix alloy. Thus, the surface of SiC particles was coated with a thin silicon-dioxide(SiO_2) layer before casting. Then, SiC particles added into the semi-solid matrix alloy at 600°C. An argon atmosphere was maintained over the melting to reduce the oxidation. Secondly, hot extrusion of the compocast ingots was carried out at an extrusion ratio of 10:1. Finally, samples were artificially aged(T6) at 150°C. The details of production method and T6 heat treatment were described in the previous study[19].

TABLE 1 : Chemical composition of the matrix alloy used in the present study

	Composition (%)							
Material	Si	Mg	Cu	Mn	Ni	Zn	Fe	Al
Matrix Alloy	6.62	0.67	0.013	0.027	0.008	0.08	0.298	Bal.

The effect of the porosities on corrosion behavior was examined using the potentiodynamic polarization technique. All electrochemical measurements were carried out in 3.5% wt. NaCl aqueous solution at room temperature in a pyrex glass cell and proceeded according to ASTM standard(G5-94)[20]. The potentiodynamic polarization curves were obtained by using an AgCl/Ag reference electrode and a Pt counter-electrode. The exposed area of the samples was about 1cm^2. The potential was controlled with a Wenking PGS95 potentiostat(BANK). After polarization tests, the specimens were cleaned mechanically and ultrasonically for metallographic observations. The SEM observations carried out by using Jeol 6400 scanning electron microscope(SEM).

RESULTS AND DISCUSSION

The chemical composition of the matrix alloy used in the present study is given in TABLE 1. Reinforcement distribution was non-homogenous in the composites and including diverse porosities. Typical porosities in the microstructure of the composites are shown in figure 1. Clusters and voids can be seen in the microstructures. Meanwhile, the formation of the type porosities is inevitable when the composites produced by stir-casting technique.

Overall porosity contents of unreinforced matrix alloy and composites are given in TABLE 2. The details of the porosity measurement are given in the previous study[8].

It can be said that, locally decomposed cathode-anode zone trigger the corrosion mechanism for cluster type porosities. Noble components gathered due

TABLE 2. Porosity values of the matrix alloy and composites in as-cast and extruded conditions

Materials	Porosity (vol. %)	
	As-cast	Extruded
Matrix Alloy	1,35	1,09
Al–10% SiC$_p$	4,70	1,26
Al–20% SiC$_p$	13,86	1,89

to clustering, increase the ratio of local cathode area at the region where these types of porosities are exist. As a result, the small anode/big cathode corrosion mechanism occurs which is the most detrimental and where the pits extend in depth[21-23]. This process takes progress quickly and continues until the reinforcements ejected from the matrix. The following reactions take part in this process;

$$Al \rightarrow Al^{3+} + 3e^- \quad (1)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (2)$$

After oxidizing of Al^{3+} ions according to reaction 1 and 2, it will react with Cl^- ions and transform to aluminum chloride according to reactions 3, 4 and 5. This may cause an increase in the solubility of the thin oxide film[24-25].

$$Al(OH)_3 + Cl^- \rightarrow AlCl(OH)_2 + OH^- \quad (3)$$

$$AlCl(OH)_2 + Cl^- \rightarrow AlCl_2OH + OH^- \quad (4)$$

$$AlCl_2OH + Cl^- \rightarrow Al^{3+} + 3Cl^- + OH^- \quad (5)$$

As a result of an increase in the ion concentration; (a) the solubility of passivity accelerator O_2 will decrease, (b) the interior cluster pH will decrease compared to the solution pH, (c) interior cluster potential will anodize as a result of a decrease to negative values compared to the matrix potential, (d) the increase in the positive ions exist in the cluster and the H^+ ions will cause to form preferential areas to Cl^- ions exits in the solution and results in diffusion of the Cl^- ions to the clusters. And this brings into existence an effect of increase in the corrosion of aluminum[15-16, 24, 26-27].

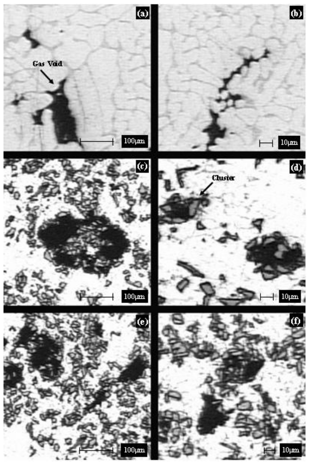

Figure 1: Clusters and voids in the microstructure of (a-b) matrix alloy, (c-d) 10% vol. SiC$_p$ composite, (e-f) 20% vol. SiC$_p$ composite

The absent of low resistant ascent areas of the electrons formed in consequence of dissolution at the surface and an increase in H^+ ion concentration in the cluster will cause the cluster act as an anode and cathode. The bottom parts of the clusters, where the lowest oxygen concentration and highest positive charge and acidity are exist, will anodize. Because of the nearness of the cathode areas, where H_2 leaves out ($H^+ + e^- \rightarrow ½H_2$)[24-25, 28], to the bottom parts the interior cluster pH will increase from bottom to the upper part. As a result, while Al^{3+} ions increase at the bottom parts of the cluster, the oxidation tendency increases at the upper parts which have high pH values. Thus, while the cluster begins to close, the diffusion of Cl^- ions decreases (Figure 2).

Consequently, the oxide film at the surface prevents the O_2 entrance and the corrosion rate will decelerate or even stop with the ascent of H_2. The high positive charge concentration at the parts of the covered cluster will attract the Cl^- ions and thus the Cl^- ion concentration in the oxide film will increase compared to other areas. Thus, these areas exhibit locally higher solubility of the oxide film and surface conductivity. In other words, the cluster may re-activate at any moment. At the advanced stage of the corrosion, before the cluster closed temporary, if another particle comes out, the corrosion continues around these particles (Figure 3a). Because, SiC is a

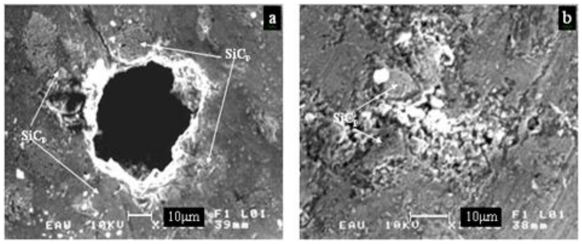

Figure 2: Closure steps of cluster: (a) beginning of closure, (b) finish of closure

Figure 3: Preferentially corrosion process progressed around SiC particle

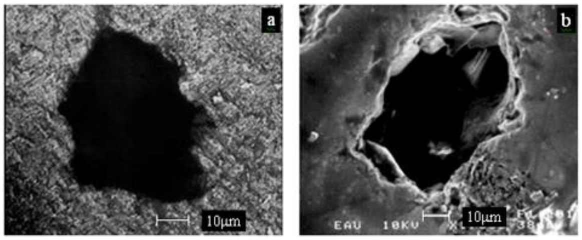

Figure 5: Micrographs of matrix: (a) Before corrosion test and (b) Nucleated pits around of porosity that exposed potential just above E_{corr} potential

noble material and will not undergo corrosion(Figure 3.b)[12, 15]. Thus, localized corrosion in Al matrix alloy progresses quickly and in-depth. This type of corrosion known as “pitting” and even it cause less material loss, it may damage the construction. As a result, this kind of constitutions may affect the normal pitting corrosion behavior of the material.

It has been shown[13] that the corrosion resistance will decrease with increasing the porosity ratio. Thus, while pressureless casting methods are used to produce MMCs, it is important to use secondary processes such as extrusion in order to eliminate the porosity. However, as expected these secondary processes will affect the corrosion behaviour of the composites. Figure 4a, demonstrates the effect of extrusion on the microstructure and reinforcement distribution, and figure 4b, the corrosion developed around the cluster porosities after the extrusion process.

Figure 5(a-b) demonstrates the nucleation of pits around the gas porosity in Al-Si-Mg matrix alloy which has been exposed to a potential over the corrosion potential.

Gas porosities existing on the metal surface are areas where electrolyte is stagnating and make the oxygen transfer difficult. As a result, these areas will act as anode and surroundings of the porosities will act as cathode[12]. When the matrix was polarized indeed anodically the E_{corr} potential, performed SEM examinations confirmed the presence of pits on the surface at this potential(Figure 6a). By increasing the potential, these porosities filled with corrosion products and passivity the upper surface(Figure 6b).

High positive charge concentration at the parts of the covered porosity attracts Cl^- ions and Cl^- ion concentration in the oxide film increase compared to other areas. Thus, these areas exhibit locally higher solubility of the oxide film and surface conductivity. Consequently, porosities act as preferential corrosion areas. Also, under these corrosion products, due to the absent of sufficient oxygen the corrosion continues[22-24, 28].

CONCLUSIONS

SEM observations show that the porosity significantly affects the corrosion behavior of Al-Si-Mg/SiC_p composites in 3.5% wt. NaCl solution. It can be seen that, locally decomposed cathode-anode zone trigger the corrosion mechanism for cluster type porosities. In addition, due to SiC is a noble material and will not undergo corrosion, localized corrosion in Al matrix alloy progresses quickly and

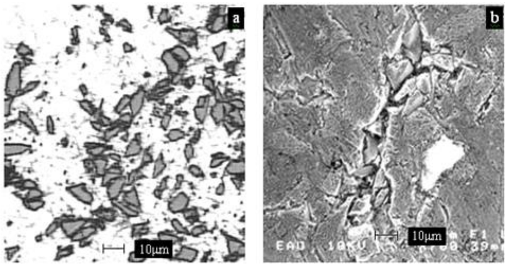

Figure 4: (a) The effect of extrusion on porosity, (b) The corrosion effect on the extruded porosities

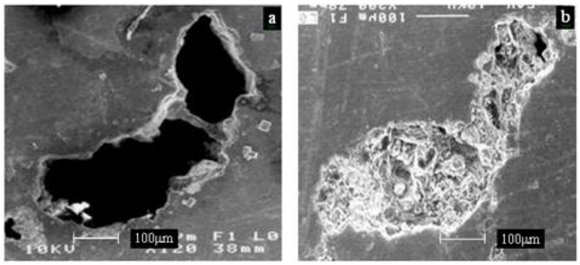

Figure 6: Gas porosity corrosion (a) At E_{corr} potential, and (b) Above E_{corr} potential

in-depth. Gas porosities exist on the metal surface are areas where the electrolyte is stagnating and cause the oxygen transfer difficult. As a result, these areas act as anode and surroundings of the porosities act as cathode.

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