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**PAPER 23**

## **DEGRADATION OF $Al_4C_3$ IN Al-Mg-Si/ $SiC_p$ COMPOSITES EXPOSED TO MOIST ENVIRONMENTS**

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### ABSTRACT

In this work the degradation of metal/composite (M/C) interfaces in Al-Mg-Si/ $SiC_p$  composites exposed to moist environments was investigated. The formation of  $Al(OH)_3$  at the M/C interface indicated the development of  $Al_4C_3$  during processing. It was found that at room temperature  $Al_4C_3$  slowly reacts with moisture in the atmosphere. As a result, the composite undergoes degradation with the degradation rate increasing logarithmically with time. In particular, it was found that the kinetics of degradation is influenced by the atmospheric conditions and the air quality.

**Keywords:** Al/ $SiC_p$  composites; pressureless infiltration; degradation of  $Al_4C_3$ .

### RESUMEN

En este trabajo se investigó la degradación de la interfase metal/composito (M/C) en compósitos Al-Mg-Si/ $SiC_p$  expuestos a condiciones ambientales. La formación de la fase  $Al(OH)_3$  en la interfase M/C indicó la presencia de  $Al_4C_3$  formada durante el procesamiento. Se encontró que la fase  $Al_4C_3$  reacciona lentamente con la humedad atmosférica a temperatura ambiente. La velocidad de degradación incrementa logarítmicamente con el tiempo. En particular, la cinética de degradación está influenciada por las condiciones atmosféricas y la calidad del aire.

## INTRODUCTION

During the processing of the Al/SiC<sub>p</sub> composites via alloy melting there are undesirable reactions which can lead to the formation of aluminium carbides, Al<sub>4</sub>C<sub>3</sub> [1-6]. In general, the development of Al<sub>4</sub>C<sub>3</sub> phases is strongly influenced by the temperature, holding times and silicon content in the matrix [1-7]. Hence, a number of technological approaches have been considered to address this problem, including: (a) control of time and temperature parameters, (b) modification of the metal matrix chemistry (Si, Li, etc.) and (c) use of metallic and oxide coatings on the ceramic reinforcements. In addition, due to its inherent advantages, the oxidation of SiC has been seriously considered by various workers [2,5-7]. As a result, the method of adding SiO<sub>2</sub> particles into SiC<sub>p</sub> performs is actually considered as a new route in order to avoid the formation of the Al<sub>4</sub>C<sub>3</sub> phase [8].

Several studies have shown that Al<sub>4</sub>C<sub>3</sub> has several detrimental effects such as (a) degradation of the reinforcement strength and the interfacial strength, (b) instability of the reaction product Al<sub>4</sub>C<sub>3</sub> in environments such as water, methanol, HCl, etc. [1-4], due to the hydrophilic nature of this phase. Park *et al* [9] investigated the formation of Al<sub>4</sub>C<sub>3</sub> and the propensity to its dissolution when exposed to de-ionized water environments. In their work, they found that when water is in direct contact with Al<sub>4</sub>C<sub>3</sub> dissolution is relatively fast resulting in pitting of the SiC/6061 Al interface.

The degradation of Al<sub>4</sub>C<sub>3</sub> under moist atmospheres has not yet been investigated in detail. Hence, in the present work the degradation of Al<sub>4</sub>C<sub>3</sub> in the presence of atmospheric moisture at room temperature was investigated. In particular, the changes occurring in the M/C interfaces were characterized by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive x-ray (EDX) and x-ray diffraction (XRD).

## EXPERIMENTAL

In this work Al/SiC<sub>p</sub> composites were fabricated by pressureless infiltration in the temperature range of 950-1100°C and times of 0 to 60 min using an Al-10Mg-12Si alloy and cylindrical SiC<sub>p</sub> performs with 50% porosity. After furnace cooling, first in a nitrogen atmosphere down to 550°C and then in air to room temperature, MMC samples were prepared for chemical and microstructural analyses.

Formation of Al<sub>4</sub>C<sub>3</sub> was intentionally promoted by infiltration at relatively high temperatures (1100°C) and long processing times (60 min). Since the outer surface of the cylindrical preform is the area exposed to liquid aluminum samples infiltrated for the longest time periods are thus expected to be the most susceptible to the formation of aluminum carbide (Al<sub>4</sub>C<sub>3</sub>).

Accordingly, MMC's were sectioned longitudinally to produce slabs for microstructural characterization. Specimens were mounted and polished

using standard metallurgical procedures and the analysis was carried out using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive x-rays (EDX) and x-rays diffraction (XRD, CuK $\alpha$  radiation). In order to identify and reveal the morphology of the reaction products at the metal/composite interface, specimens were electrochemically etched (DC-5V-3A) with an aqueous solution of HNO<sub>3</sub> (33 vol%).

## RESULTS AND DISCUSSION

The microstructure of the resultant MMC's interfaces was analyzed 20 days, 4 months and 17 months after infiltration. SEM results of the resultant M/C interfaces indicate that a notable dissolution of the SiC particles took place in the composite. Figure 1, shows the resultant M/C interface of a specimen exposed to 1100°C and 60 min, the attack of SiC particles is indicated by the arrow in this figure. XRD analyses of the MMC composite show that the presence of two new phases, Mg<sub>2</sub>Si and AlN. Yet, there are no diffraction peaks corresponding to the harmful aluminum carbide phases (see Figure 2).

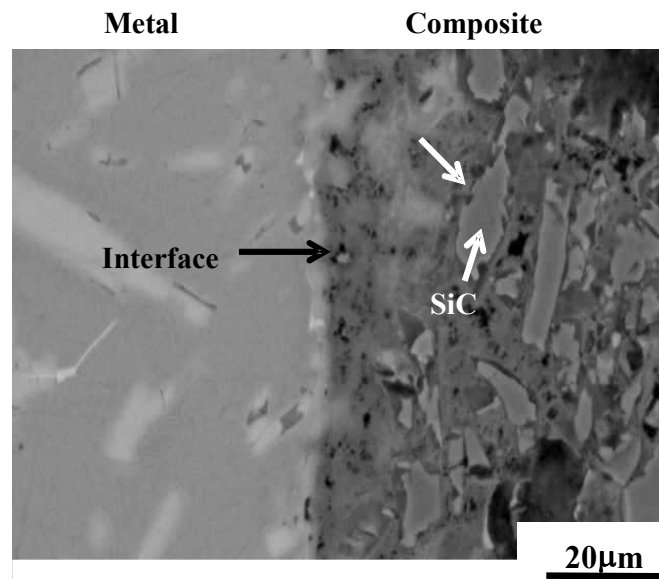
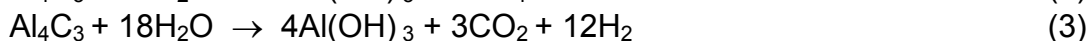


Figure 1. Scanning electron photomicrograph of the M/C interface taken 20 days after the infiltration trials of a specimen processed at 1100°C for 60 min.

Four months after infiltration, the MMC a reaction zone characterized by a porous phase was observed in the M/C interface. X-ray diffraction of the porous phase indicated the presence of aluminum hydroxide Al(OH)<sub>3</sub> at the M/C interface (see Figure 3). The development of Al(OH)<sub>3</sub> at the M/C interface can be explained by the reaction of Al<sub>4</sub>C<sub>3</sub> with moisture from the atmosphere according to [4, 9-10]:



Since the composite specimens were not immersed in water, but exposed to the ambient atmosphere, it is expected that the formation of  $\text{Al}(\text{OH})_3$  is closely related to the interaction of  $\text{Al}_4\text{C}_3$  with moisture. According to Kosolapova, reaction (2) takes place slowly at room temperature with the liberation of methane gas [10].

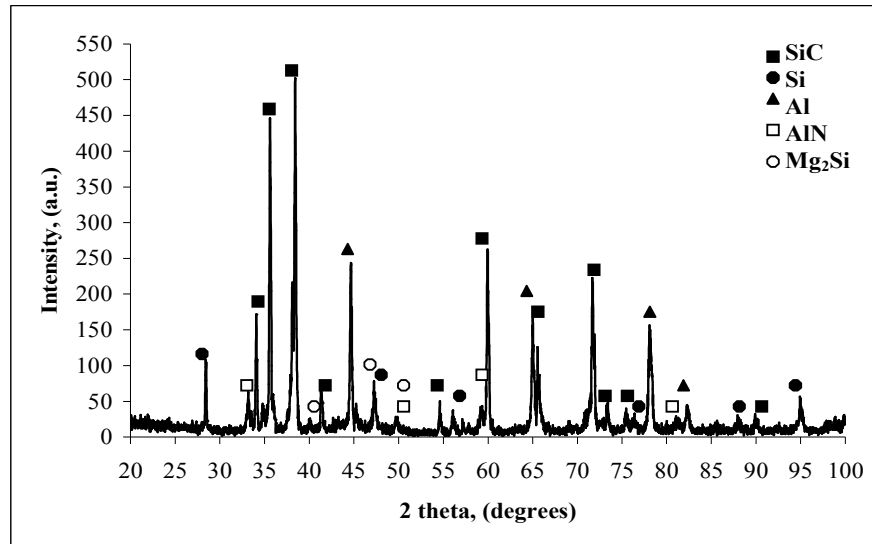


Figure 2. X-ray diffraction pattern in the composite specimen processed at 1100°C for 60 min (20 days after the infiltration trials).

Alternatively, Park *et al.* suggest that  $\text{CO}_2$  gas is evolved during the interaction of aluminum carbide with water according to reaction (3). They attribute this to observations of bubbles emerging from the polished surface of a SiC/6061 composite material [9].

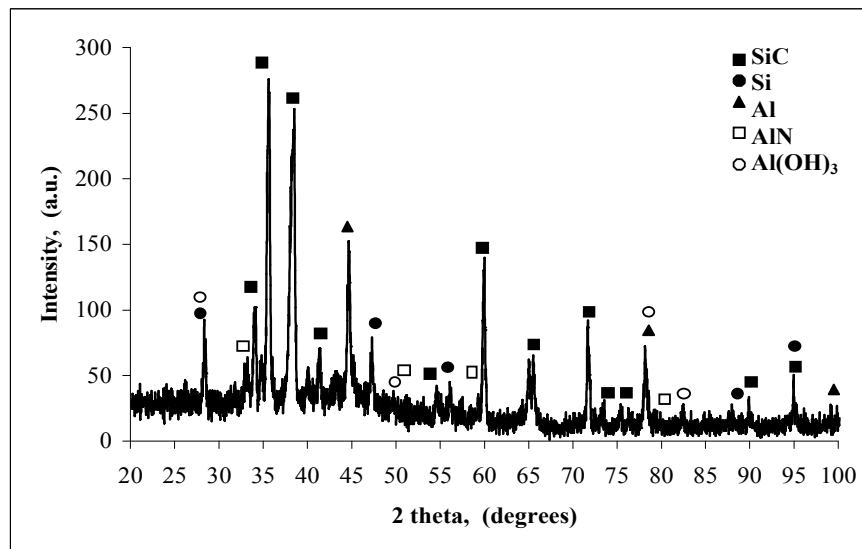


Figure 3. X-ray diffraction pattern of the powder formed in the reaction zone at the metal/composite interface (4 months after the infiltration trials).

Figure 4 SEM is an SEM micrograph of the M/C interface 17 months after infiltration trials of a specimen processed at 1100°C for 60 min. Notice that in this case the reaction zone is characterized by a volume expansion due the reaction between the  $Al_4C_3$  and moisture from the atmosphere. Since the density of  $Al_4C_3$  is lower than that of SiC and Al, upon carbide formation there is a net volume expansion. This volume expansion induces mechanical stressing of the M/C interface due to dilatational strains associated with  $Al_4C_3$  formation. In turn, this leads to degradation of the interfacial strength [11].

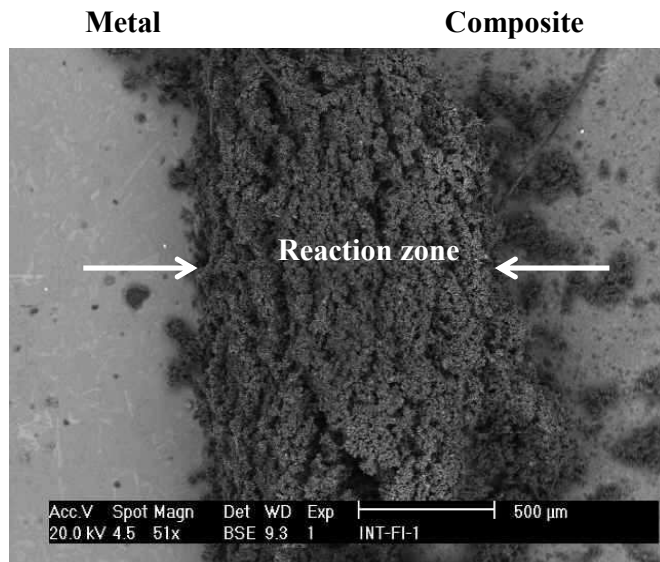


Figure 4. Scanning electron photomicrograph taken 17 months after the infiltration trials in the specimen processed at 1100°C for 60 min.

Figure 5 shows graphically the thickness of the reaction zone as a function of the exposure time under atmospheric moisture. The extension for the reaction zone increased from 0.65 mm (after 4 months) to 1.04 mm (after 17 months). According to this figure, the thickness of the reaction zone increases with the exposure time to the environment in a logarithmic way.

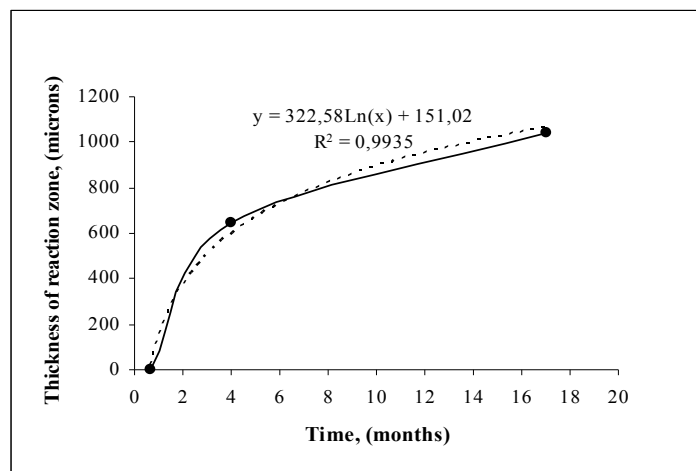


Figure 5. Plot of thickness of reaction zone vs. exposure time in atmospheric moisture.

Figures 6a-b are SEM micrographs of the metal/composite interface of a specimen processed at 1100°C for 60 min and electrochemically etched. It is evident that there is partial dissolution of the SiC particles (indicated by arrows) by liquid aluminum at preferential SiC planes. According to the literature, pits on the SiC particles have been observed but (0001) SiC planes exhibit increasing resistance to the attack by liquid aluminum [12].

In the specimens fabricated at 1050°C and 1100°C it was found that there is degradation of the M/C interface at room temperature. However, the degradation of  $Al_4C_3$  with atmospheric moisture is in general slow and it depends on the chemistry of the air and moisture.

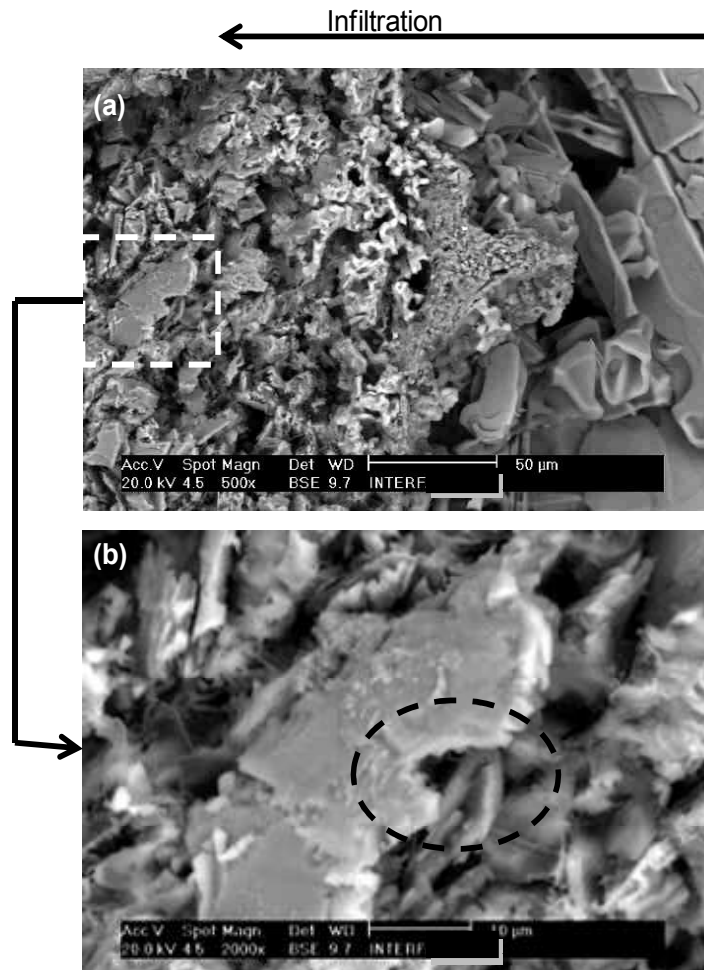


Figure 6. Scanning electron photomicrograph showing the metal/composite interface of composite electrochemically etched.

## SUMMARY AND CONCLUSIONS

Results from this investigation show that the unwanted  $\text{Al}_4\text{C}_3$  phase was not identified shortly after the processing of the composites. Nevertheless, the presence of  $\text{Al}(\text{OH})_3$  4 and 17 months after the infiltration tests reveals that the unwanted  $\text{Al}_4\text{C}_3$  phase actually forms under the processing conditions employed. It is worth noting however, that structurally the  $\text{Al}(\text{OH})_3$  phase can be present in various forms. It was found that thickening of the reaction zone versus time follows a logarithmic tendency. Apparently, the kinetics of the  $\text{Al}_4\text{C}_3$  degradation at the M/C interfaces are affected by the atmospheric conditions, such as temperature and air quality. In addition, partial dissolution of the SiC particles can be explained by some facets of SiC particles being more resistant than others to the attack by liquid aluminum.

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