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## EFFECT OF SIO<sub>2P</sub> INTO SIC<sub>P</sub> PREFORMS ON THE MICROSTRUCTURE AND THE KINETICS OF PRESSURELESS INFILTRATION BY AN ALUMINUM ALLOY

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### Effect of SiO<sub>2p</sub> into SiC<sub>p</sub> Preforms on the Microstructure and the Kinetics of Pressureless Infiltration by an Aluminum Alloy

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#### RESUMEN

Se investigó el efecto de la presencia de partículas de SiO<sub>2</sub> en preformas de SiC<sub>p</sub> sobre la microestructura y la cinética de infiltración no asistida de preformas cilíndricas de SiC<sub>p</sub> por la aleación Al-12.04 Si-10.3 Mg (% e.p.). Se encontró que la presencia de SiO<sub>2</sub> tiene un efecto benéfico al prevenir la formación de fases indeseables Al<sub>4</sub>C<sub>3</sub> en el compósito. No obstante, también disminuye el grado de infiltración por la modificación de las características de porosidad de la preforma. Se encontró que a las máximas condiciones de prueba (1100°C y 60 min.), se alcanzó un porcentaje de área infiltrada del 96% (sin SiO<sub>2</sub>), de 40% para el sistema 2 (con SiO<sub>2</sub> como "cuarzo") y de 48% para el sistema 3 (con SiO<sub>2</sub> como "cristobalita"). Sin embargo, la interfase metal/compósito de muestras correspondientes al sistema 1, exhibe una zona de reacción la cual se atribuye al desarrollo de hidróxido de aluminio (Al (OH)<sub>3</sub>) formado por la reacción de Al<sub>4</sub>C<sub>3</sub> con la humedad del ambiente. La ausencia de Al<sub>4</sub>C<sub>3</sub> en las interfases de muestras de los sistemas 2 y 3 se explica por el suministro de Si al sistema durante la reacción de la SiO<sub>2</sub> con la aleación de aluminio.

#### ABSTRACT

The effect of SiO<sub>2</sub> particles into SiC<sub>p</sub> preforms on the microstructure and the kinetics of pressureless infiltration of cylindrical preforms by the alloy Al-12.04 Si-10.3 Mg (wt. %) was investigated. It was found that the presence of SiO<sub>2p</sub> has a beneficial effect since it prevents the development of the unwanted Al<sub>4</sub>C<sub>3</sub> phase. Nonetheless, it also diminishes the degree of infiltration by modifying the characteristics of the porous microstructure. It was found that at the maximum tests conditions (1100°C and 60 min) the percentage of area infiltrated was 96 % for system 1 (without SiO<sub>2p</sub>), 40 % for system 2 (SiO<sub>2</sub> "quartz") and 48 % for system 3 (SiO<sub>2</sub> "cristobalite"). However, the metal/composite interface of specimens corresponding to system 1 exhibits a reaction zone attributed to development of aluminum hydroxide (Al(OH)<sub>3</sub>) formed by reaction of Al<sub>4</sub>C<sub>3</sub> with moisture in the atmosphere. The absence of Al<sub>4</sub>C<sub>3</sub> in systems 2 and 3, that is explained in terms of the Si supplied to the system during the reaction of SiO<sub>2</sub> with the aluminum alloy.

#### 1. INTRODUCTION

A number of technological approaches have been used by several investigators to overcome the problem of the development of harmful reaction products ( $Al_4C_3$ ) at the reinforcement/matrix interface during the processing of Al/SiC composites by the route with the molten metal. A great interest there exists in using alloying elements of high reactivity such as Si and Li in aluminum to diminish the tendency to the formation of  $Al_4C_3$ [1-10]. Particularly the use of silicon to control the negative reactions at the interface has been widely accepted and practiced, not only as an alloying element, but also as a coating on the SiC reinforcements. The popularity of silicon as compared to lithium can be explained in terms of both, economical and technological standpoints.

The role that silicon plays in the Al/SiC system can be viewed form two different standpoints. It has been extensively reported that it reduces the activity of aluminum, thereby suppressing a direct contact between the SiC reinforcement and the molten metal. Moreover, the presence of free Si on the surface of SiC significantly reduces the contact angle between the molten aluminum and the substrate[11].

As far as coatings on the SiC reinforcements are concerned, several technological approaches involving a variety of materials have been reported in the literature [4,9,11,15]. For instance, metallic coatings (Cu, Ni, Si, etc.), salts ( $K_2ZrF_6$ ), silicates ( $Na_2SiO_3$ ), and metallic oxides ( $Al_2O_3$ , TiO<sub>2</sub>, MgO, etc.) have been successfully applied. However, due to its inherent advantages, the oxidation of SiC reinforcements has attracted the attention of many researchers [4,7-8,12-16]. An additional benefit to the protection of the SiC from dissolution, is that the reaction of SiO<sub>2</sub> results in the formation of new phases that are believed induce a strong bonding between the matrix and the reinforcement and provide stability to the composite. Specifically, when the aluminum matrix contains Mg, the reaction of SiO<sub>2</sub> with the liquid alloy provides the Si necessary to suppress the formation of  $Al_4C_3$ [12-16].

Nonetheless, a major drawback there exists by the passive oxidation method because of its difficulty to control the thickness and uniformity of the  $SiO_2$  layer, particularly when oxidizing a bed of SiC powders[15-16]. In addition the passive oxidation itself represents an extra stage and cost to the processing.

Due to the inherent advantages that represent having  $SiO_2$  in the system and the difficulties associated to forming coatings by oxidation, the development of alternative routes to take advantage of its beneficial effect is highly desirable. In the present work, the effect of having  $SiO_2$  in the system not as a layer on the  $SiC_p$  reinforcements, but as powders, was investigated.

#### 2. EXPERIMENTAL

#### 2.1 Materials and procedures

Three types of cylindrical preforms (2.0 cm high x 2.0 cm in diameter) were prepared with SiC and  $SiC/SiO_2$  powders according to Table 1, which shows the alloy/reinforcement systems studied in the experiment.

ALLOY REINFORCEMENT (wt. %)		SYSTEM	
Al-10.3Mg-12.04Si	SiC <sub>P</sub>	1	
	$SiC_P + SiO_{2P}$ (quartz reactive grade)*	2	
	$SiC_P + SiO_{2P}$ (cristobalite reactive grade)*	3	

 Table 1.
 Alloy/Reinforcement systems used in the experiment

Results from characterization of the powders using a COULTER LS particle size analyzer, a gas picnometer and a scanning electron microscope are shown in Table 2.

Powder	Purity	Average Particle size (µm)	Density (g/cm <sup>3</sup> )	S.S.A. <sup>*</sup> (cm <sup>2</sup> /ml)	Morphology
SiC-α (6-H "Black")	Commercial	20	3.19	3,818	Irregular
SiO <sub>2</sub> (quartz)	R. grade (Spectrum)	3	2.72	34,785	Agglomerates
SiO2 (cristobalite)	R. grade (Fluka)	4	2.49	21,013	Agglomerates

Table 2. Characteristics of the powders used for the preparation of preforms

<sup>\*</sup>Specific surface area.

According to table 1, the powders were mixed thoroughly with 10 % dextrin and distilled water. Then, the mixtures were placed in a steel die and compacted to produce preforms with 50% porosity. The preforms were dried at 125°C in a forced air drier for 2 hours, and then cured at 225°C for 2 more hours. A preform, together with 40±1.0 g of the aluminum alloy (Al-12.04Si-10.3Mg) in the form platelets that were ultrasonically cleaned in acetone, was placed in a ceramic container that was previously coated with boron nitride.

Infiltration trials were performed in a horizontal tube furnace with a 6.5 cm diameter alumina tube that was closed at both ends with end-cap fittings to control the process atmosphere. Both fittings were sealed with O-rings and the system worked at a very slight over-pressure to ambient. A K-type thermocouple was inserted in one end of the tube to control the sample temperature. The system (mold-preform-metal) was placed in the center of the tube and heated in ultra high purity argon atmosphere at a rate of 15°C/min up to 600°C. During heat up, any residual binder was volatilized and removed from the system in the flowing argon. At 600°C, in order to

enhance the wetting of the SiC particles by the aluminum alloy, the atmosphere was changed to ultra high purity nitrogen and the system was heated at a rate of  $15^{\circ}$ C/min to different test temperatures ( $950 \pm 5$ ,  $1000 \pm 5$ ,  $1050 \pm 5$  and  $1100 \pm 5^{\circ}$ C). Once the furnace reached the test temperature, the system was held isothermally for various test times (0, 20, 40 and 60 min) in nitrogen atmosphere.

After furnace cooling to room temperature in nitrogen atmosphere, the cylindrical composites were removed from the furnace and prepared for chemical and microstructure analysis. Since the outer surface of a cylindrical preform  $(SiC_p \text{ or } SiC_p/SiO_{2p})$  is the area exposed to the liquid aluminum the longest time period, it is thus expected to be more susceptible to the formation of the unwanted phase aluminum carbide  $(Al_4C_3)$ . Consequently, the soundness of the composite depends in a large extent on the condition of the Metal/Composite (M/C) interface. Accordingly, the composites were sectioned longitudinally and prepared for microstructure characterization of the M/C interface. Specimens were mounted and polished using standard metallurgical procedures, and the analysis was done using optical microscopy, scanning electron microscopy (SEM), energy dispersive x-rays (EDX) and x-ray diffraction (XRD, CuK $\alpha$  radiation).

The degree of infiltration was evaluated measuring the percentage of the total cross sectional area of a cylindrical preform that was filled by the aluminum and the infiltrated area in each specimen was measured using an optical microscope provided with an image analyzer system (Image-Pro Plus 4).

#### **3.- RESULTS AND DISCUSSION**

#### 3.1 Degree of infiltration

In Fig. 1, plots of infiltrated cross-sectional area vs. time for various processing temperatures corresponding to the system 1 are shown. For all holding times at 950°C, no infiltration is observed. At the temperature of 1000°C, the degree of infiltration increases gradually, reaching a maximum value of infiltrated area of 10 % up to 60 min. For the test at 1050°C, the degree of infiltration also increases gradually, up to 24% after 60 min. The corresponding isotherm at 1100°C shows a rapid increase in the degree of infiltration during the first 20 min after which the increase rate decreases. The total area infiltrated after 60 min reached a maximum value of 96%.



Figure 1 Plot of infiltrated area vs. time for various test temperatures corresponding to system 1.

In Fig. 2, plots of infiltrated cross-sectional area vs. time for various processing temperatures and times, corresponding to system 2 (Al-Si-Mg /SiC:SiO<sub>2</sub> "<u>quartz</u>") are shown. Similar results are found in tests at 950°C, no infiltration is observed. For both temperatures, 1000 and 1050°C, infiltration begins after 20 min the ceramic preform and the molten aluminum have been in contact, which indicates the existence of an incubation period. The highest degrees of infiltration attained at these temperatures after 60 min are 13 and 17 %, respectively. With respect to the isotherm at 1100°C, the infiltration begins during heat up, before reaching the test temperature. The highest degree of infiltration attained after 60 min is of 40 %.



Figure 2 Plot of infiltrated area vs. time for various test temperatures corresponding to system 2.

In Fig. 3, plots of infiltrated cross-sectional area vs. time for various processing times and temperatures, corresponding to system 3 (Al-Si-Mg /SiC:SiO<sub>2</sub> "cristobalite") are shown. At 950°C, no infiltration is observed. For the test temperatures of 1000, 1050 and 1100°C, infiltration starts before reaching the test temperature and once it has been attained, infiltration increases gradually. The highest values of degree of infiltration attained for these temperatures after 60 min are 19, 42 and 48 %, respectively.



Figure 3 Plot of infiltrated area vs. time for various test temperatures corresponding to system 3.

It is evident that the degree and the velocity of infiltration diminish considerably when  $SiO_2$  particles are present in the system. This decrease can be attributed to the modification in the characteristics of the porous microstructure of the preforms, because still maintaining the volume fraction of porosity (50%), it is expected that introduction of a new phase with lower density and particle size, affects the permeability of the preform. An explanation on the difference observed in the degree and kinetics of infiltration when using  $SiO_2$  powders as "quartz" and "cristobalite" is beyond the scope of this paper.

#### 3.2 Metal/composite interface microstructure

Since the outer surface of the cylindrical  $SiC_p$  and  $SiC_P/SiO_{2P}$  preforms is the area exposed to the liquid aluminum the longest time period, it is expected to be more susceptible to the formation of aluminum carbides. Accordingly, the M/C interfaces of the specimens were analyzed by XRD. The x-ray diffraction patterns of the specimens shown in Figure 4 reveal the absence of aluminum carbide in all three systems. In all specimens analyzed, the phases Mg<sub>2</sub>Si, SiC, Si, Al and AlN were detected. However, the spinel phase MgAl<sub>2</sub>O<sub>4</sub> was also detected in system 2 and 3. The spinel phase was formed by the reaction of SiO<sub>2</sub> with aluminum alloy containing magnesium, during the process of infiltration according to the following [12-16] :

$$2 \operatorname{SiO}_{2(s)} + a \operatorname{Al}_{(l)} + Mg_{(l)} \rightarrow MgAl_2O_{4(s)} + 2 \operatorname{Si}_{(s)}$$



Figure 4 XRD patterns of composites of different systems processed at 1100°C for 60 min holding time.

In order to study the effect of  $SiO_2$  into  $SiC_P$  performs, the M/C interfaces of specimens from the three systems were microscopically analyzed 2900 hours after the infiltration tests. In Fig. 5 Optical photomicrographs of the specimens examined are shown.

While the interface in specimens from system 2 and 3 are apparently in good condition, the interface of the specimen from system 1 exhibits a reaction zone. The reaction zone in system 1 is attributed to the development of aluminum hydroxide (Al (OH)<sub>3</sub>) formed by the reaction of the unwanted  $Al_4C_3$  phase present in the composite with moisture in the atmosphere, according to the following equations [4,11]:

 $Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$  $Al_4C_3 + 18H_2O \rightarrow 4Al(OH)_3 + 3CO_2 + 12H_2$ 

Since the reaction zone in specimens from system 1 can only be explained by the presence of aluminum carbide, the absence of this phase in the XRD patterns can be attributed to the amount of  $Al_4C_3$  present in the specimens.  $Al_4C_3$  was present in such amounts that were below the limits of detection of the diffractometer.

The condition of the M/C interface reflects in some extent the efficacy of the incorporation of  $SiO_2$  particles into  $SiC_p$  in preventing or retarding the development of the unwanted  $Al_4C_3$  during infiltration of the ceramic preforms by an Al-Si-Mg alloy.



Figure 5 Optical photomicrographs corresponding to the M/C interface for systems 1, 2 and 3 (from top to bottom), taken 2900 hours after infiltration trials. The specimens were processed at 1100°C for 60 min.

#### 4. SUMMARY AND CONCLUSIONS

Results from this investigation reveal that the presence of  $SiO_{2p}$  in the Al-Si-Mg/SiC system has a beneficial effect since it prevents the development of the unwanted  $Al_4C_3$  phase. Nonetheless, it also has a parallel and negative effect because it diminishes the degree of infiltration and the kinetics of incorporation of the liquid aluminum into the porous preform. The decrease in the degree and kinetics of infiltration can be explained in terms of the modification of the characteristics of the porous microstructure. It was found that at the maximum tests conditions (1100°C and 60 min) the percentage of area infiltrated was 96 % for system 1 (without SiO<sub>2p</sub>), 40 % for system 2 (SiO<sub>2</sub> "quartz") and 48 % for system 3 (SiO<sub>2</sub> "cristobalite"). However, the metal/composite interface of the specimen from system 1, analyzed 2900 hours after processing, exhibited a reaction zone attributed to development of aluminum hydroxide (Al(OH)<sub>3</sub>) formed by reaction of Al<sub>4</sub>C<sub>3</sub> with moisture in the atmosphere. The absence of Al<sub>4</sub>C<sub>3</sub> in systems 2 and 3, is explained in terms of the Si supplied to the system during the reaction of SiO<sub>2</sub> with the aluminum alloy and confirms the efficacy of the presence of SiO<sub>2</sub> powders in the system.

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