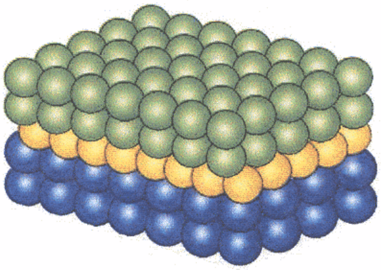

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MICROSTRUCTURAL MODIFICATION OF Al/SiC$_P$ COMPOSITES TO AVOID Al_4C_3 VIA PRESSURELESS INFILTRATION

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RESUMEN

Ha sido posible minimizar la formación de productos de reacción perjudiciales en compósitos Al/SiC$_p$ por la presencia de silicio en el sistema, debido a la modificación en la microestructura. La modificación de la microestructura ocurre durante la infiltración reactiva de preformas SiC$_P$:SiO$_{2P}$ con la aleación Al-10Mg-12.5Si (% e.p.), en atmósfera de nitrógeno. Los compósitos se caracterizaron por DRX, MO y MEB con facilidades para microanálisis por EDX. Se encontró que debido a la presencia de SiO_2 en el sistema, es posible evitar la formación las fases perjudiciales (Al_4C_3) a altas temperaturas y tiempos largos de procesamiento. La formación de la fase $MgAl_2O_4$ (termodinámicamente estable), se atribuye a la alta reactividad de la sílice (SiO_2) con la aleación de aluminio utilizada, generando el Si necesario para evitar la formación de la fase Al_4C_3. El material resultante es un compósito multifásico de matriz de aluminio. Adicionalmente, se encontró que debido a la formación de la fase $MgAl_2O_4$, la densidad de los compósitos se incrementa ligeramente (< 3 %).

ABSTRACT

It has been possible to minimize the formation of harmful reaction products in Al/SiCp composites by the presence of silicon in the system, due to the modification of the microstructure. Modification of the microstructure occurs during the reactive infiltration of SiC$_P$:SiO$_{2P}$ preforms by the Al–10Mg-12.5Si (wt.%) alloy under nitrogen atmosphere. The composites were characterized by XRD, OM, SEM and energy dispersive X-rays (EDX). It was found that due to the presence of SiO_2, it is possible to avoid the formation the harmful phases (Al_4C_3) at high temperatures and long processing times. Formation of the phase $MgAl_2O_4$ (thermodynamically stable), is attributed to the high reactivity of silica (SiO_2) with the aluminum alloy, producing the Si necessary to avoid the formation of the Al_4C_3 phase. The resulting material is a multiphase aluminum matrix composite. In addition, it was found that due to the $MgAl_2O_4$ formed, the density of the composites is slightly increased (< 3 %).

1.- INTRODUCTION

In spite of many efforts carried out to notably enhance and optimize the wettability in the Al/SiC system, it is well known that there are still barriers that have hindered viable production of Al/SiC composites by fabrication routes that involve prolonged processing times such as pressureless infiltration. Two main drawbacks typically reported when using this particular route are the potential development of harmful reaction products (Al_4C_3) at the Al/SiC interface from the dissolution of SiC by liquid aluminum and the presence of considerable levels of retained porosity. Several approaches have been used by a number of investigators to address both problems; these include: i) control of the processing parameters time and temperature, ii) alteration of the metal matrix chemical composition and, iii) coatings on the ceramic reinforcement (SiC) [1-3].

A great interest there exists in using alloying elements of high reactivity such as Si and Li to diminish the tendency to the formation of Al_4C_3 [4-7]. Particularly, the use of silicon to control of the reactions at the Al/SiC interface has been widely accepted and practiced, not only as an alloying element, but also as a coating on the SiC reinforcements [4-6].

The role that silicon plays in the Al/SiC system can be viewed from different standpoints. On the one hand, it has been reported that the presence of free silicon on the surface of SiC significantly reduces the contact angle between the molten aluminum alloy and the substrate [8]. On the other hand, it has been considered that reduces the activity of aluminum, thereby suppressing a direct reaction between Al and SiC [9].

Due to their inherent advantages, coating methodologies have been lately the subject of an intense investigation. A coating on the reinforcement may have contributions in improving the wetting of the ceramic by the molten metal and/or decreasing the amount in the harmful reaction products and [10].

A variety of materials have been used as coatings such as: a) metals (Cu, Ni, Si, etc.), b) salts (K_2ZrF_6), c) silicates (Na_2SiO_3), d) metallic oxides (Al_2O_3, TiO_2, MgO, etc.), e) colloidal silica and f) SiO_2 formed by the passive oxidation of the SiC reinforcement [10-14].

Owing to its simplicity, the passive oxidation technique has attracted the attention of many researchers [10, 13, 14]. The benefits associated to this technique are that SiO_2 reacts with the matrix to form new phases that are believed induce a strong bonding between the matrix and the reinforcement and provide stability to the composite. Moreover, when the aluminum matrix contains magnesium, the reaction of SiO_2 with the aluminum alloy provides the Si necessary to avoid the formation of Al_4C_3. Nonetheless, a major drawback in the passive oxidation method is its difficulty to control the thickness and uniformity of the layer of SiO_2, particularly when oxidizing a bed of powders. In addition, the passive oxidation itself also represents an extra stage and cost to the processing. Due to the inherent advantages that represent having a layer of SiO_2 on the SiC reinforcements and the difficulties associated to forming such coating, the development of alternative routes to exploit its beneficial effect is highly desirable.

In this work, an alternative approach consisting of the incorporation of SiO_2 particles into the SiC_p preforms with the aim of preventing or retarding the formation of unwanted phases (Al_4C_3) and reducing residual porosity is investigated.

2.- EXPERIMENTAL

Materials and procedures

Two 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:

Table 1. Alloy/Reinforcement systems used in the experiment.

Alloy (% e. p.)	**Ceramic reinforcement**	**System**
Al-10.3Mg-12.04Si	SiC_P (As received)	A
Al-10.3Mg-12.04Si	$SiC_P + SiO_{2P}$ (cristobalite reactive grade)*	B

* SiC_P:SiO_{2P} (7:1)

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

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

Powder	**Purity**	**Average Particle size (μm)**	**Density (g/cm^3)**	**S.S.A.* (cm^2/ml)**	**Morphology**
SiC-α (6-H "Black")	Commercial	20	3.19	3,818	Irregular
SiO_2 (cristobalite)	R. grade (Fluka)	4	2.49	21,013	Agglomerates

*Specific surface area

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 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. 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 heated in ultra high purity argon atmosphere at a rate of 15°C/min up to 650°C.

During heat up, any residual binder was volatilized and removed from the system in flowing argon. At 650°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°C/min up to 1100°C. At this temperature, the system was held isothermally for 60 min in nitrogen atmosphere.

After furnace cooling to room temperature in nitrogen, the cylindrical composites were removed from the furnace and prepared for chemical and microstructure analysis. Since the outer surface of a cylindrical (SiC_P and SiC_P:SiO_{2P}) preform is the area exposed to the liquid aluminum the longest time period, it is thus expected to be more susceptible to the formation of aluminum carbide (Al_4C_3). Consequently, the soundness of the composite depends in a large extent on the condition of the composite/metal (C/M) interface. Accordingly, the composites were sectioned longitudinally to produce slabs for microstructure analysis. 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, CuKα radiation).

3.- RESULTS AND DISCUSSION

Composite/metal interface characterization

In Fig. 1 x ray diffraction patterns from the analysis of the C/M interface of specimens from both systems are shown.

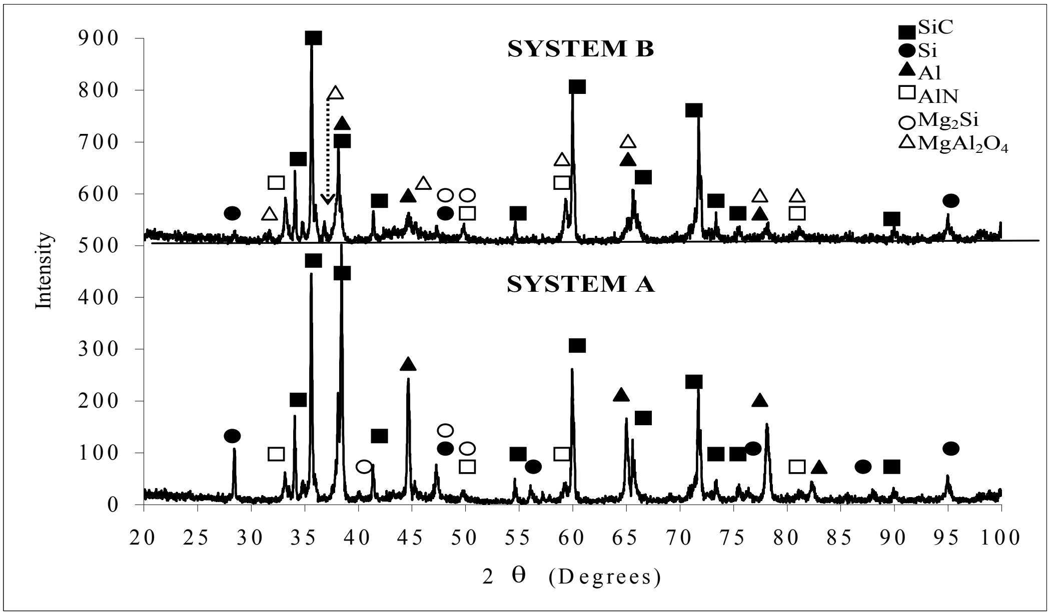


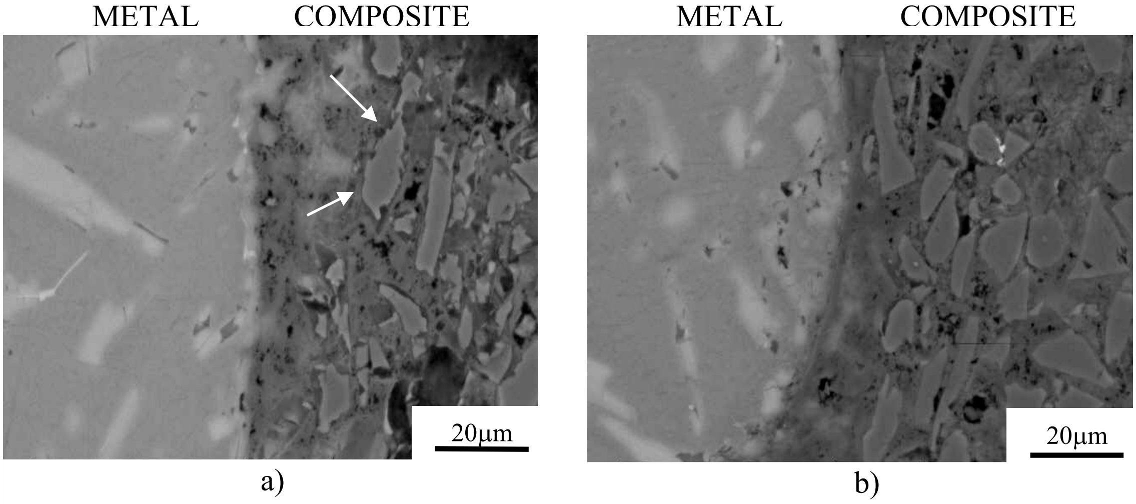
Figure 1. XRD patterns (CuKα) of composites: (a) system A, (b) system B. Both specimens were processed at 1100°C for 60 min.

It is worth noting that in both patterns, the unwanted phase aluminum carbide was not revealed. However, the phases Mg_2Si and AlN were detected in both systems. Furthermore, in system B the $MgAl_2O_4$ was also identified.

Precipitation of Mg_2Si has been attributed to the reaction between the silicon released by the dissolution of the SiC reinforcements and the magnesium present in the system. Kon Bae Lee et al, fabricated Al/SiC_p composites using an Al-Mg alloy and found that the age hardening response of the composites was due to the reaction between the silicon dissolved with the magnesium in the alloy [15]. Mg_2Si has been identified in Al/SiC composites fabricated by the pressureless infiltration method and the compocasting technique [15, 16].

As far as the AlN phase is concerned, a number of authors have discussed that its presence is associated to the formation of magnesium nitride (Mg_3N_2) in the system due to the interaction of Mg with nitrogen in the atmosphere. Formation of Mg_3N_2 in the system has been considered for various investigators as a key factor for pressureless infiltration [2, 17, 18].

In Fig. 2, SEM photomicrographs corresponding to C/M interfaces in specimens from both systems A and B are shown. Fig. 2(a) shows that partial dissolution of the SiC particles (indicated by arrows) took place in the specimen from system A. On the other hand, although processed under the same conditions, it seems that in the specimen from system B, no degradation of the SiC reinforcement occurred. The fact that XRD patterns did not reveal the presence of Al_4C_3, but partial dissolution of the reinforcement is observed in Fig. 2 (a), suggests that aluminum carbides may be present but in such quantities below the limits of detection by the XRD technique. It is thus apparent that incorporation of SiO_{2p} into the SiC_p preforms positively affects the microstructure condition of the composite.



a) b)

Figure 2. SEM photomicrographs corresponding to the Composite/Metal interface: (a) system A, (b) system B. Both specimens were processed at 1100°C for 60 min.

Suppression of the undesirable phase (Al_4C_3) and the presence of the aluminum spinel phase ($MgAl_2O_4$) in specimen from system B, can be explained according to the following. The SiO_2 particles may react with the magnesium containing aluminum alloy [14]:

$$2\ SiO_{2\,(s)} + 2\ Al_{(l)} + Mg_{(l)} \rightarrow MgAl_2O_{4\,(s)} + 2\ Si_{(s)} \qquad \text{(I)}$$

A paramount consequence of reaction (I) is that SiO_2 may act as a Si supplier to avoid or retard the formation of Al_4C_3 in the Al/SiC system:

$$4\ Al + 3\ SiC \rightarrow Al_4C_3 + 3\ Si \qquad \text{(II)}$$

Another important benefit of the method of incorporating SiO_2 into the system is that the new phase $MgAl_2O_4$ is thermodynamically more stable than the unwanted phase.

Due to the formation of new phases in the system, the density of the composites was modified. The measured densities of the resultant composites are 2.44 and 2.51 g/cm^3 for the systems A and B, respectively.

In order to verify the effectiveness of the method of incorporating SiO_2 particles into the SiC_p preforms, the C/M interfaces of specimens from both systems A and B were microscopically analyzed some time after the infiltration trials. In Fig. 3 optical photomicrographs of two specimens examined 2900 hours after infiltration tests are shown. While the interface in specimen from system B is apparently in good condition, the interface of the specimen from system A exhibits a reaction zone. The white phase observed in the reaction zone (in Fig. 3(a)) is attributed to the formation of aluminum hydroxide (Al $(OH)_3$). Aluminum hydroxide is formed when the unwanted phase Al_4C_3 present in the composite reacts with moisture in the atmosphere, according to the following equations [19,20]:

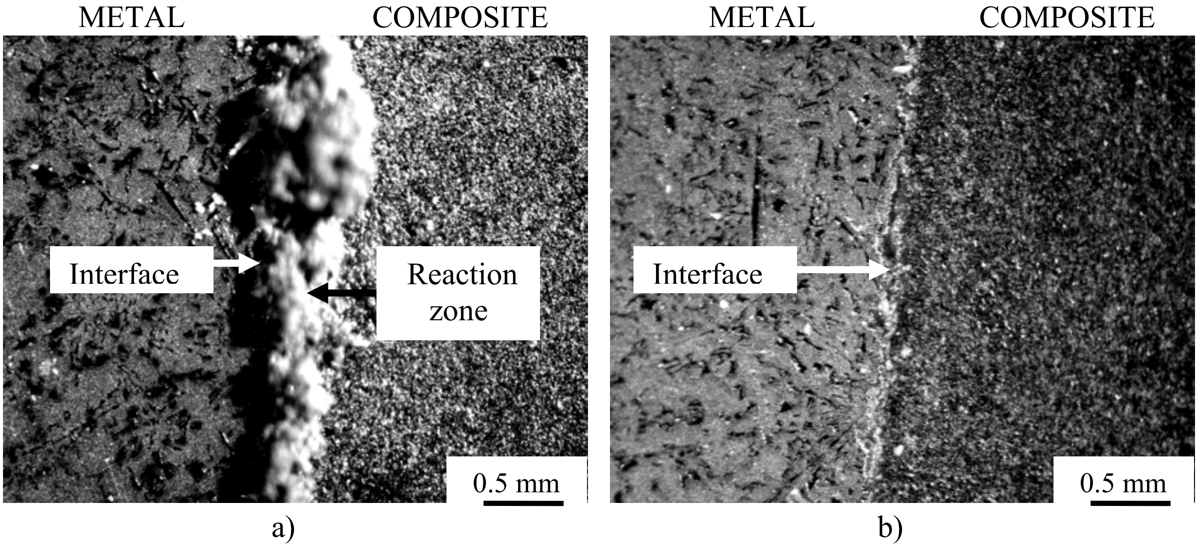
$$Al_4C_3 + 18\ H_2O \rightarrow 4\ Al(OH)_3 + 3\ CO_2 + 12\ H_2 \qquad \text{(III)}$$

$$Al_4C_3 + 12\ H_2O \rightarrow 4\ Al\ (OH)_3 + 3CH_4 \qquad \text{(IV)}$$

It is apparent from the interface condition of specimen B in Fig. 3(b) that the incorporation of SiO_2 particles helps in preventing the development of the unwanted aluminum carbides at the Composite/Metal interface during infiltration. This fact guarantees in some extent, the soundness of the inner composite.

5.- CONCLUSIONS

The addition of SiO_2 particles to the Al/SiC system plays a three-fold role: 1) helps minimizing the harmful reaction products (Al_4C_3), 2) promotes the formation of thermodynamically stable phases ($MgAl_2O_4$) and, 3) slightly increase the density of the composites. The absence of Al_3C_4 and formation of phase $MgAl_2O_4$ in the system B, confirms the efficacy of the microestructural modification during the pressureless infiltration of the aluminum alloy into the SiC_p ceramic preform. Due to the presence of new phases, the density of resultant composite in the system B was increased only in 3 %, with respect to the system without SiO_2 additions (system A).



a) b)

Figure 3. Optical photomicrographs corresponding to the Composite/Metal interface for systems a) A and b) B, taken 2900 hours after infiltration trials. Both specimens were processed at 1100°C for 60 min.

Acknowledgements

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