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RESUMEN

La fase nitruro de aluminio (AlN) fue formada in situ durante el procesamiento por infiltración no asistida (percolación/capilaridad) de preformas de SiC/SiO₂ para producir compósitos Al/SiC/Al₂O₃. Se prepararon preformas rectangulares (4cm x 4cm x 0.5 cm) por compactación de una mezcla de polvos de SiO₂ y de SiC. El tamaño promedio de ambos polvos fue de 20 µm. Las preformas fueron infiltradas por una aleación de aluminio (Al- 9.53 % e.p. Mg-10.2 % e.p. Si) en atmósfera de argón y nitrógeno y las pruebas se realizaron a las temperaturas de 1100 y 1150 °C durante tiempos de prueba de 45, 50, 55 y 60 min. Las muestras obtenidas fueron analizadas por difracción de rayos X (DRX), microscopía electrónica de barrido (MEB) y por espectroscopía por dispersión de energía (EDX). La fase AlN se formó a ambas temperaturas; sin embargo, mientras que a 1100 °C el contenido de AlN incrementa con el tiempo, a 1150 °C disminuye. Las condiciones óptimas para maximizar la formación de AlN son 1100 °C y 55 minutos.

ABSTRACT

Aluminum nitride as reinforcement (AlN) was formed in situ during the processing by pressureless infiltration (percolation /capillary effect) of SiC/SiO₂ preforms to produce Al/SiC/Al₂O₃ composites. Rectangular preforms (4cm x 4cm x 0.5 cm) were prepared by compaction of a mixture of SiO₂ and SiC powders. The average particle size of both powders was 20 µm. Preforms were infiltrated by an aluminum alloy (Al-9.53 wt. % Mg-10.2 wt.% Si) in argon and nitrogen atmosphere and the trials were carried out at the temperatures of 1100 and 1150 °C for 45, 50, 55 and 60 min. Specimens were analyzed by X-ray diffraction (XRD), scanning electronic microscopy (SEM) and energy dispersive X-rays (EDX). AlN was formed at both temperatures; however, whilst at 1100 °C AlN content increases with time, at 1150 °C AlN content decreases. Optimum conditions to maximize AlN formation are 1100 °C and 55 min.



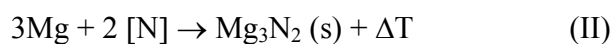
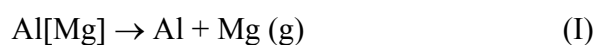
1. INTRODUCTION

Current research on the processing of aluminum matrix composites has displayed a prominent progress by shifting to the second generation approaches, in which reinforcing materials are formed in situ. In contrast to the first generation processing routes which involve the incorporation of separately produced ceramic reinforcements, in situ processes involve the development of ceramic reinforcing materials such as carbides, nitrides or borides during composite fabrication. A number of inherent advantages make the in situ processing of composite materials of relevant importance. Expected advantages of in situ processing approaches include: capability to produce a variety of reinforcement morphologies, flexibility to synthesize either ductile or ceramic in nature reinforcements, finer reinforcement sizes and, since the interfaces are formed in situ, improved compatibility between the matrix and the reinforcement. Moreover, they offer the potential for economical and continuous processing [1-3].

Within the variety of reinforcements that can be processed in situ, aluminum nitride (AlN) has become a promising one. In recent years, AlN/Al composites have attracted the attention of many researchers. One of the major advantages of AlN with respect to traditional reinforcements such as Al₂O₃ and SiC is that it is better wetted by aluminum and does not decompose in molten aluminum as SiC does. Thus, negative interface reactions do not represent critical issues. In addition, AlN can enhance the strength, modulus, wear resistance, and refractory nature of aluminum alloy matrix as SiC and Al₂O₃ do. Composites with a high volume fraction of AlN have the potential for improved thermal conductivity, low thermal expansion and moderate stiffness. Despite of the many advantages offered by AlN as reinforcement, AlN/Al composites have not achieved their full potential. When starting with AlN powders, challenging problems arise not only because AlN powders are expensive, but also because they are relatively reactive. Thus, in situ processing of AlN/Al composites is an attractive fabrication route [4-6].

There are currently two major approaches to produce AlN as reinforcement in aluminum, namely direct nitridation and indirect nitridation. The first method is a direct liquid-gas reaction to produce solid particles and consists of aluminum reacting with nitrogen-bearing gases directly to form AlN precipitates. The second involves Mg in the melt and consists of formation of Mg₃N₂ as an intermediate nitride, followed by a substitution or replacement reaction to produce AlN [4].

During indirect nitridation, magnesium vaporizes from the melt during holding at the processing temperature and is prematurely lost from the alloy. Being in vapor phase, it reacts with the nitrogen-containing atmosphere through an exothermic reaction to form Mg₃N₂, typically identified as a greenish-yellow powder. Then, Mg₃N₂ particles precipitate into the melt, where the substitution reaction to form AlN occurs. The sequence of reactions that take place is as follows [4]:





The above series of reactions has been considered alternatively from another perspective, specifically, as a mechanism through which Mg is recycled back into the melt to enhance spontaneous infiltration of Al_2O_3 and SiC preforms [7, 8].

In this work, the in situ formation of AlN during the processing of $\text{Al}/\text{SiC}_p/\text{Al}_2\text{O}_{3p}$ composites by the pressureless infiltration method has been studied. Production of the $\text{Al}/\text{SiC}/\text{Al}_2\text{O}_3$ composites involves in situ formation of the Al_2O_3 reinforcements into $\text{SiC}_p/\text{SiO}_{2p}$ preforms.

2. EXPERIMENTAL PROCEDURE

Experiment

In this work, the effect of the processing temperature and time on the in situ formation of AlN was investigated. The parameter temperature was studied at two levels (1100 and 1150 °C) and the processing time was investigated at four levels (45, 50, 55 and 60 min), according to Table 1.

Table 1 Total number of tests

	45 (min)	50 (min)	55 (min)	60 (min)
1100 °C	P1	P2	P3	P4
1150 °C	P5	P6	P7	P8

Materials and procedures

Commercial SiC powders and SiO_2 powders were used to prepare rectangular preforms (4 cm x 3 cm x 0.5 cm). The average particle size of both powders was 20 μm . SiO_2 powders were obtained by calcining rice hulls at 800 °C for two hours. Predetermined amounts of the SiC and SiO_2 powders were thoroughly mixed and compacted to produce 30 v% SiC/10 v% SiO_2 and 60 % porosity preforms. A preform together with about 36 g of the aluminum alloy in the form of plates was placed into a ceramic container previously coated with boron nitride. In order to promote incorporation of the aluminum alloy by both percolation and capillary action, aluminum plates were placed on top (percolation) and at the bottom (capillary effect) of the preforms. The chemical composition of the aluminum alloy specifically designed for this investigation is shown in Table 1.

Table 2 Chemical composition (wt. %) of the alloy used in the experiment

Si	Mg	Total other elements	Al
10.2	9.53	0.119	Balance

Infiltration trials were performed in a horizontal tube furnace with a 6.5 cm diameter alumina tube provided with end-cap fittings to control the process atmosphere. The preforms were heated in ultra high purity argon at rate of 15 °C/min up to the test temperature. At this temperature, in order to enhance the wetting of the SiC particles by the liquid aluminum, the atmosphere was switched to ultra high purity nitrogen and the system was held isothermally for the established test time as illustrated schematically in Fig. 2.

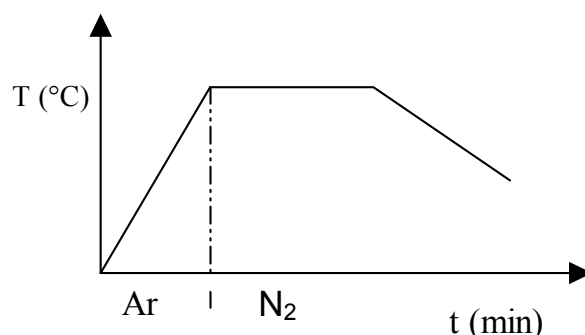


Figure 2 Thermal cycle used during infiltration tests

After cooling to room temperature in nitrogen atmosphere, the infiltrated slabs were removed from the furnace and prepared for microstructural characterization. Specimens were sectioned and polished using standard metallurgical procedures, and microstructural characterization was performed using optical microscopy, scanning electron microscopy (SEM), energy dispersive X-rays (EDX) and X-ray diffraction (XRD).

3. RESULTS AND DISCUSSION

Results from XRD tests showed that the AlN phase was formed at both test temperatures, 1100 °C and 1150 °C. In addition, the presence of the MgAl₂O₄ spinel was also revealed at both temperatures. Moreover, at 1150 °C Mg₂Si and the unwanted Al₄C₃ phase were also detected. In Figs. 3 and 4, XRD patterns (obtained using CuK α radiation) of the composites produced at 1100 °C and 1150 °C for various test times are shown, respectively. The occurrence of the Mg₂Si phase and MgAl₂O₄ spinel can be explained as follows.

Formation of Mg₂Si in Al/SiC composites fabricated by the pressureless infiltration method and the compocasting technique has been reported by other authors [9, 10]. Precipitation of Mg₂Si was attributed to the reaction between the silicon released by the dissolution of the SiC reinforcements and the magnesium present in the system. In the work by Kon Bae Lee et al, since composites were fabricated from an Al-Mg alloy, the age hardening response of the composites was attributed to the dissolved silicon which further reacted with the magnesium in the alloy [9]. In the present work, at 1150 °C, formation of Mg₂Si coincided with development of the unwanted Al₄C₃ phase.

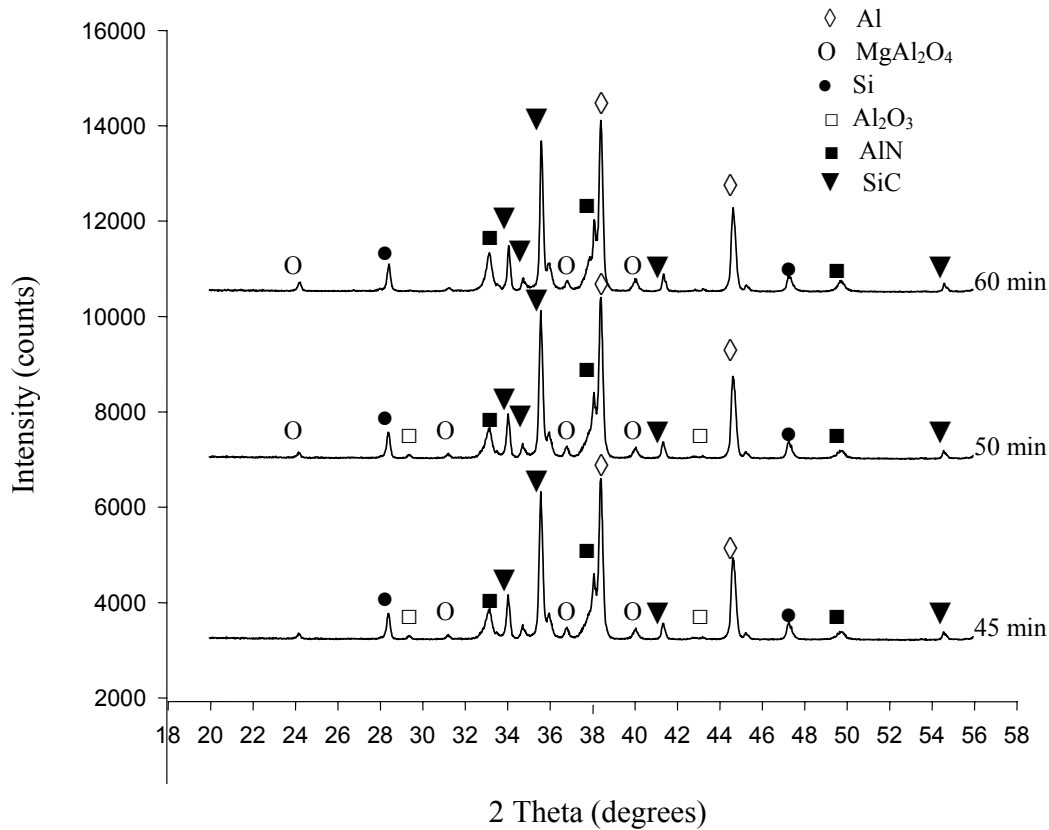


Figure 3 XRD patterns showing the phases formed in the composites at 1100 °C.

Formation of MgAl_2O_4 spinel has been related to the magnesium content in the system. While formation of the MgAl_2O_4 spinel is promoted at low Mg contents (lower than 4 %) and high temperatures, relatively high Mg contents (5%) favor the formation of MgO in addition to MgAl_2O_4 . MgAl_2O_4 may be formed through several possible reactions [11, 12]; however, due to the presence of SiO_2 in the system, its occurrence is best described by the following equation:



The amount of AlN formed during the processing of the composites, was quantified using the Sietronic XRD program. This program allows a semiquantitative determination of a given phase, based on the areas under of the reflections. In Fig. 5 results from the semiquantitative analysis in specimens processed at both temperatures for various times are shown.

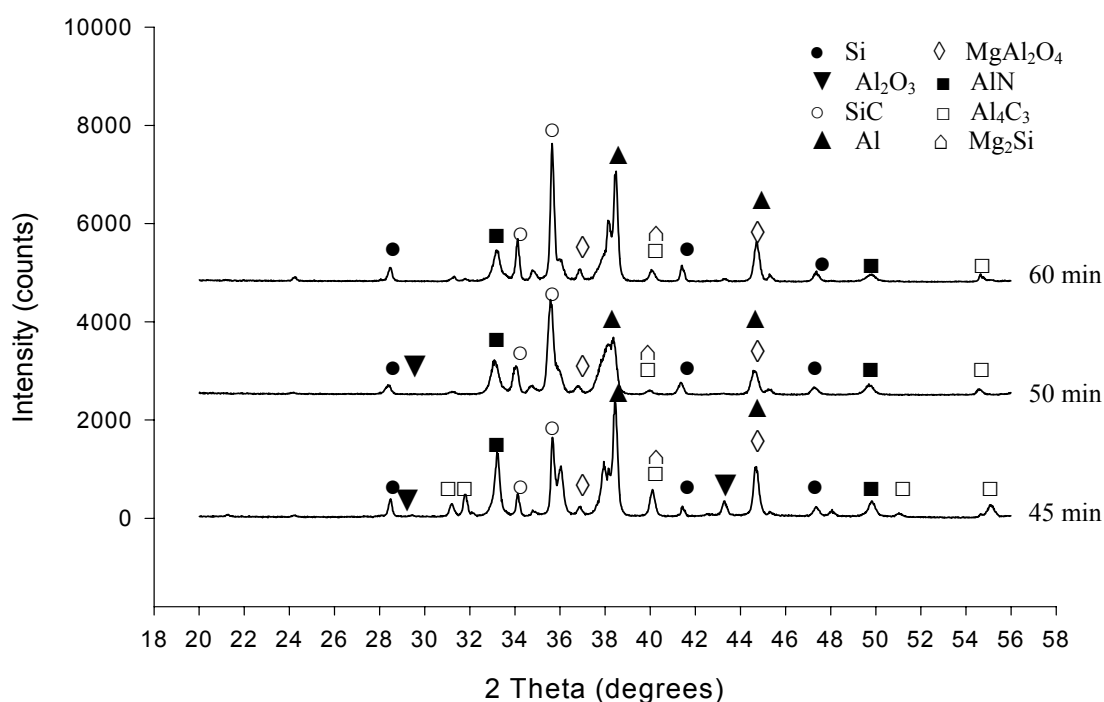


Figure 4 XRD patterns showing the phases formed in the composites at 1150 °C.

According to Fig. 5 whereas at 1100 °C AlN content increases with time, at 1150 °C it decreases. Furthermore, at the highest test temperature, formation of AlN is favored at short times. At 1150 °C and 45 min the amount of AlN already formed is the maximum. However, the unwanted Al₄C₃ phase is also formed. A discussion on the conditions at which formation of Al₄C₃ can be suppressed has been reported elsewhere [13].

Decrease in the amount of AlN formed at 1150 °C with time can be attributed to a depletion of Mg in the system. According to equations (II) and (III), formation of magnesium nitride (Mg₃N₂) is a prerequisite for the production of AlN. On the other hand, it has been frequently reported that magnesium is lost from the system by evaporation [4, 6, 7]. Thus, the higher the temperature and the longer the processing times, the higher the amount of Mg lost from the system and consequently the lower the amount of AlN formed. Indeed, the kinetics of infiltration is found to be significantly affected by Mg loss from the system [14]. It has been reported that AlN is found as small precipitates and as a thin film on the surface of the reinforcing phase [15]. Fig. 6 is a SEM photomicrograph showing the presence of AlN as short fibers surrounding the SiC particles within the residual porosity of composites.

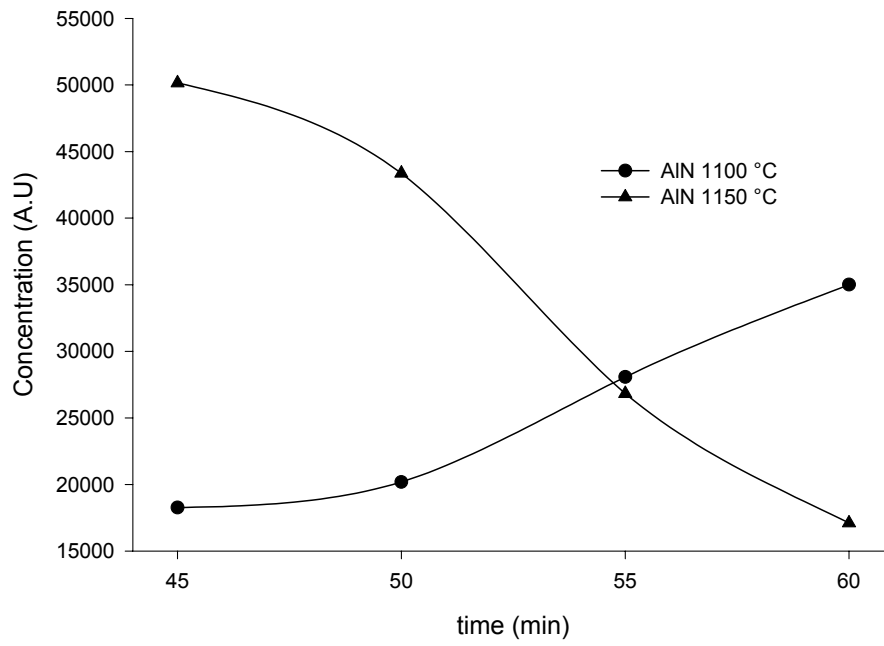


Figure 5 Variation of AlN content in the composites with time at 1100 °C and 1150 °C.

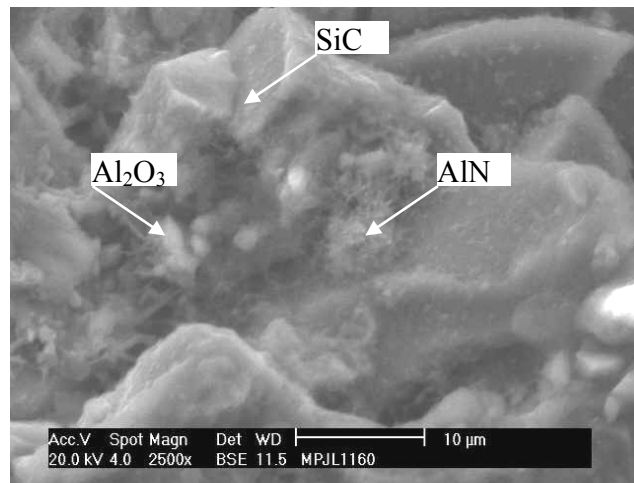


Figure 6 SEM photomicrograph of a composite processed at 1100 °C for 50 min.

4. SUMMARY AND CONCLUSIONS

It has been found that the AlN phase can be formed in situ during the production of Al/SiC_p/Al₂O_{3p} composites by the combined percolation/capillary effect, both at 1100 and 1150 °C. However, at 1150 °C AlN content decreases with time and formation of the unwanted Al₄C₃ phase is also favored. It has also been found that typically AlN is formed as short fibers surrounding the SiC particles within the residual porosity. The optimum parameters to favor formation of AlN and Al₂O₃ and yet, to avoid Al₄C₃ development are 1100 °C and 55 min test time.

Acknowledgements

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