Synthesis of Al$_2$O$_3$/Ti$_3$Al composites by *in-situ* displacement reactions

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The employment of aluminothermic reactions of displacement as an alternative for the production of Al$_2$O$_3$/Ti$_3$Al composite materials has been investigated. Compacted samples from an intensely ground mixture of powders of TiO$_2$ + Al$_2$O$_3$ + Al were sintered at 1500ºC during 1 hour by hot pressing in an argon atmosphere. The TiO$_2$ is used as predecessor to generate *in-situ* Al$_2$O$_3$ via its reduction by means of metallic Al. Al reacts also in a simultaneous way with the reduced titanium to form an intermetallic alloy of the type Ti$_x$Al$_y$. The Al$_2$O$_3$ employed in the precursor materials is used as a way for the dissipation of the heat build-up during the aluminothermic reduction of the TiO$_2$. The results of the characterizations indicate that Al$_2$O$_3$-based composite materials were obtained with reinforcement particles of Ti$_x$Al$_y$. The microstructure of these materials is dense, fine and homogeneous. The preliminary characterization of the microstructure and its composition features subsequent to the cycle of *in-situ* processing are presented here.

Key words: Al$_2$O$_3$/Ti$_3$Al, Composites, *In-Situ*, Displacement Reactions.

Introduction

The incorporation of ductile phases in ceramic matrices generally results in significant increases of the fracture toughness of the composite [1,2]. The reinforcement happens though the plastic deformation of the metallic particles. That appear in the top of the cracks. The improvement by the reinforcement will depend on the properties of the union in the ceramic-metal interfacial zone, the flow properties of the metal and of the particles that are present in the transverse section in front of the crack. Recently, many Al$_2$O$_3$-based systems have been studied, where different metals of reinforcement have been used such as; nickel [3], aluminium [4] or copper [5], all these systems have showed a decrease of their yiel stress and therefore an increase in their fracture toughness. Lately, a new development in which aluminum-based intermetallic (Ni$_3$Al, Ti$_3$Al, Fe$_3$Al, etc.) particles have been incorporated in Al$_2$O$_3$-matrix ceramics has been created successfully [6-12]. The attractive properties of these intermetallic alloys include low densities, high melting points, good mechanical properties and resistance to corrosion at high temperatures. Nevertheless, difficulties in the manufacture of these composite materials have been an important reason for a limitation in the use of these materials. Considerable efforts have been made in improving the technologies of processing these materials to increase their applications. Among other methods for example one has tried to fabricate that type of composite materials by mechanical alloying [6], by reactive sintering [7] and by direct oxidation of metal [13]. However, all these methods are expensive and difficult to control due to the strongly exothermic reactions that take place during the processing. In this study, a combination of technologies such as; mechanical alloying and sintering by hot pressing of TiO$_2$ + Al$_2$O$_3$ + Al powder mixtures for the *in-situ* synthesis of Al$_2$O$_3$/Ti$_x$Al$_y$ composite materials is analyzed.

Experimental procedure

Samples of 30 g of aluminium ($\approx$5 mm), a-Al$_2$O$_3$ ($\approx$1 mm) and TiO$_2$ ($\approx$1 mm) mixed in a at 3/12/15 g were ground by them dry at 300 rpm during 12 h, using balls of 3Y-TZP in a container of polyethylene. The sum of the starting materials; Al, TiO$_2$ and Al$_2$O$_3$ fits to the necessary amounts to form the products indicated in reaction (1). After the grinding, the powder mixtures were passed across a 325 μm mesh to undo possible agglomerates. These powders were formed into cylindrical samples 2 cm in diameter by 0.3 cm in thickness by means of uniaxial pressing at 270 MPa. Later these samples were sintered by hot pressing in an argon atmosphere, a heating cycle of heating at 1 Kminute^{-1} to 1000ºC, from there heating at 10 Kminute^{-1} to 1500 ºC the sample is retained at this temperature during 1 h and then cooled to room temperature inside the furnace. The pressure used during the sintering was 40 MPa. The phases present in the material before and after the sintering were determined using X-ray diffraction. The dependence of the reaction (1) as a function of the temperature was investigated by differential thermal analysis. Density and open porosity of the materials were measured using Arquimedes' method. The microstructure of

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composites was observed with help of both optical and scanning electron microscopy. Phase quantification was effected with an image analyzer using the pictures taken with the optical microscope. Finally, the mechanical properties of the samples were measured though tests of microhardness and the fracture toughness determined by means of the method of fracture for indentation using Evans's equation [14].

$$3TiO_2 + 5Al + Al_2O_3 \rightarrow 3Al_2O_3 + Ti_3Al \qquad (1)$$

Results and discussion

Diferencial thermal analysis

The differential thermal analysis was carried out in a sample of powder following the same program of heating with which samples were sintered. The curve obtained is shown in Fig. 1. This curve presents a strongly exothermic peak at 645°C, due to the fact that the melting point of the aluminium occurs at 660°C and to the exothermic character of this event; this peak has been a partner with the aluminothermic reaction indicated in equation (1). Although, this reaction basically occurs below the melting point of the aluminium, its occurrence is very near to this for it is considered that the heat here generated creates an increase in the temperature of the sample, which surely means that it departs from the aluminum even through it has not reacted or melted, the formation of this liquid phase and the heat production can generate the appearance of porosity in the sample in agreement with the documented results by different authors [6,7].

Density and open porosity

Information on the density and open porosity of green and sintered samples appear in the Table I. Here it is possible to see that the effect of the diffusion during the sintering causes the densification of the sample. Nevertheless, if the formation of the liquid phase of aluminum is considered during heating, the
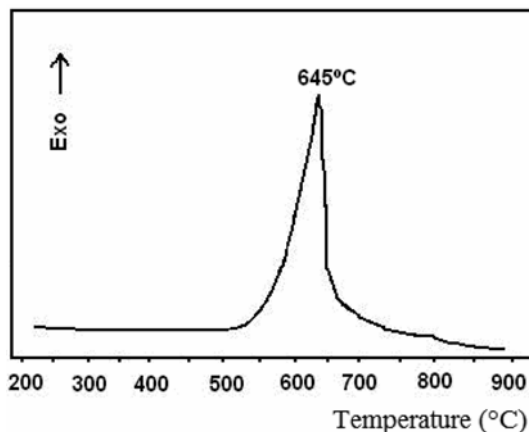
Table I. Density and open porosity values in green and sinterized samples.

	Green sample	Sinterized sample
Open porosity (%)	40	3.8
Density (g/cm³)	3.32	3.87

pore formation can be generated in the sample since aluminum is well known not to wet ceramics [12], due to this the porosity in the sample cannot be eliminated completely even by hot pressing giving values of 3.8 % porosity at the end of the sintering stage.

X-ray diffraction

The X-ray diffraction patterns of the powder mixture and the sintered sample appear in Fig. 2. In the corresponding pattern to the powder mixture it is possible to see the starting components of the mixture TiO_2 + Al_2O_3 + Al. While, that in the pattern of the sintered sample displays the formation of two new components $TiAl_3$ and Ti_3Al, the corresponding peaks to the Al and the TiO_2 have disappeared here; which allows the conclusion that the reaction (1) has taken place of in complete way during the sintering stage.

Microstructure

The microstructure obtained in Al_2O_3/Ti_3Al composites formed from a powder mixture of TiO_2+ Al_2O_3+ Al can be observed in Fig. 3. Figure 3a corresponds to an image taken in optical microscope whereas figure 3b corresponds to an image taken in a scanning electron microscope. In both images a ceramic matrix with reinforcing metallic particles homogenously distributed is seen. Metallic particles are localized mainly at intergranular zones and presents sizes less than 1 mm. With the help of energy dispersive spectroscopy microanalysis it was determined that the gray phase corresponds to the matrix is made up of Al_2O_3 and that the shining and clear particles correspond to a metallic material rich in titanium and aluminum. A quantification of phases done with the help of optical microscopy image give the
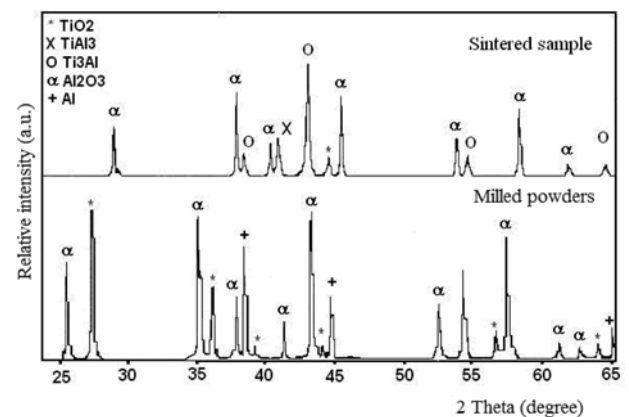

Fig. 1. Differential thermal analysis curve of the TiO_2 +Al_2O_3+Al powder mixture.

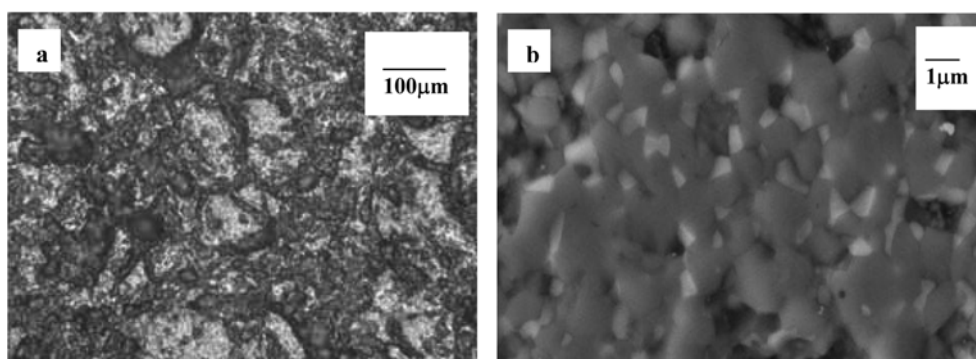**Fig. 2.** X-ray diffraction patterns of the powder mixture and sintered sample.

Fig. 3. Microstructure of the composites sintered at 1500ºC for 1 h. Phase metallic content in the composite is 12.5 vol.%. (a) Optical microscopy image, (b) Scanning electron microscopy image.

result of a material composed of 87.5% of ceramic phase and 12.5% of the metallic phase (this is without considering the porosity present in the material).

Mechanical properties

The micro-hardness and fracture toughness of the sinterized sample were 13.54+ /–0.5 GPa and 7.3+ /– 0.2 MPa · $m^{1/2}$ respectively. The mechanical properties reported in the literature for Al₂O₃/Ti₃Al composite materials with 15% volume of the intermetallic phase are of 12-14 GPa and 8 MPa · $m^{1/2}$ for micro-hardness and fracture toughness respectively [11,15]. Thus the hardness of the material fabricated here falls within the range reported in the literature. On the other hand, the value of toughness reached by the composite made here is a little smaller compared with the values reported in other studies. This difference can be attributed mainly to the smaller amount of the metallic phase and to the final density of the composite one that was obtained here in which of 3.8% porosity is present. In spite of this the mechanical properties of the composites obtained here are good, mainly in terms of the fracture toughness since this improvement is an order magnitude greater than the value of the toughness of monolithic Al₂O₃, in this sense it can be concluded that indeed the Ti₃Al intermetallic phase serves as a means of reinforcement or improvement of the fracture toughness of the Al₂O₃-based ceramic. The probable toughening mechanism is by the plastic deformation of the intermetallic particles present in the top of the cracks. Of the results obtained it is possible to hope that if a denser composite material can be made and therefore with smaller porosity this will present still better mechanical properties.

Conclusions

Al₂O₃/Ti₃Al composite materials were synthesized by means of a combination of techniques of mecahnical alloying and hot pressing of a TiO₂+ Al₂O₃+ Al powder mixture via aluminothermic *in-situ* reactions.

Al₂O₃-based composites reinforced with fine particles of Ti₃Al have been obtained with a dense, fine and homogenous microstructure.

The Ti₃Al intermetallic particles have demonstrated to be effective in the improvement of the fracture toughness of the synthesized composite materials. The probably toughening mechanism is the plastic deformation of the intermetallic particles present in the top of the cracks.

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