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Densification Improvement of Al_2O_3–SiC_w Composites by Impregnation

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Abstract: The effect of the impregnation of Al_2O_3–SiC_w composites (0, 5, 10 and 15 vol% SiC) was studied by Hg porosimetry, density measurements and SEM analysis. Samples were prepared by slip casting, precalcined, impregnated with aluminium nitrate, treated with NH_3 and pressureless-sintered in reducing atmosphere. Higher fired densities were obtained because of the lower pore volume and higher green densities resulting from the impregnation. Also, the high reactivity of the small particles filling the pores in the impregnated samples contributed to the densification improvement.

INTRODUCTION

It is well known that the addition of whiskers to a powder suspension hampers compaction and further densification.[1] Additionally, pressureless sintering in reducing atmosphere, used to avoid SiC_w oxidation, produces lower density values than other usual processing methods such as HP or HIP.[2,3] The use of an impregnation technique in order to improve the green densities of porous compacts, combined with pressureless sintering in a reducing atmosphere may represent a lower-cost method of obtaining dense Al_2O_3–SiC_w materials.

In this paper, the densification behaviour of these materials when an impregnation step is incorporated into the procedure normally used in their fabrication, is analyzed.

MATERIALS AND METHODS

Green samples of Al_2O_3 and Al_2O_3–SiC_w (5, 10 and 15 vol% SiC_w) composite materials were prepared by slip casting of an aqueous suspension of Al_2O_3 powder (Reynolds RC-HP DBM, 0·35 μm) and SiC whiskers (Tateho SCW-1). The green samples were precalcined at 950°C for 90 min.

The impregnation of the samples was made, introducing a modification to the method proposed by Kim and Lee[3] to avoid the spalling of the samples during the thermal treatment in each step. Thus, the samples were exposed to NH_3 vapors for 15 min, in order to precipitate aluminium hydroxide into the pores, instead of their immersion in a boiling ammonium hydroxide solution for 5 min. The whole procedure for impregnation includes a first step, maintaining the samples for 60 min in a saturated boiling solution of $Al(NO_3)_3$, followed by exposition to NH_3 vapors and finally, slowly calcining up to 800°C in air to obtain Al_2O_3 (γ-Al_2O_3 is the final product of the impregnation). The whole process was repeated 15 times.[4]

Samples were pressureless-sintered in a graphite-element resistance furnace (ASTRO Group 1000), under quiet He atmosphere, at 1800°C, 220 min.

The densities were determined by the Archimedes method and the relative densities were calculated based on the densities of α-Al_2O_3 (3·98 g/cm^3), SiC (3·20 g/cm^3) and γ-Al_2O_3 (3·50 g/cm^3). Pore size distributions and pore volume were analyzed by mercury porosimetry (Carlo Erba). The microstructures were examined by scanning electron microscopy (Philips 505). The chemical etching was made with 10% HF, lasting 6 min, at room temperature.

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Table 1. Pore volume of precalcined samples without and with impregnation (I)

SiC_w content (vol%)	Pore volume (mm^3/g)	
	Without I	With I
0	164·8	88·8
5	168·6	89·3
10	222·5	85·2
15	217·3	86·3

Table 2. Density values (g/cm^3) of precalcined and fired samples and percentages of theoretical densities of precalcined samples (I: impregnation)

SiC_w (vol%)	Precalcined density				Fired density	
	Without I		With I		Without I	With I
	δ	%	δ	%	δ	δ
0	2·47	62	3·10	80	3·70	3·86
5	2·29	58	2·96	77	3·36	3·40
10	2·16	55	3·06	80	3·10	3·61
15	2·10	54	2·87	76	2·72	3·07

RESULTS AND DISCUSSION

The green density of the Al_2O_3 sample was high enough (62%), according to the fabrication method (slip casting), to expect a good densification behaviour. On the other hand, the incorporation of increasing contents of SiC_w to the Al_2O_3 matrix resulted in progressively lower values of green density. All the precalcined densities were close to the starting green density values. There was no shrinkage at the temperature of precalcination (950°C) in which the strength increased, allowing handling of the sample.

Impregnation was allowed to proceed to completion, yielding bodies in which the impregnating material was distributed throughout. For the size of the samples being studied (6 × 6 × 15 mm), this represented 15 impregnations (until weight changes lower than 0·8 % were measured for one impregnation step). The impregnation behaviour of the samples containing 0, 5, 10 and 15 vol% SiC_w was similar, decreasing the effectiveness of each step with the number of impregnations. The greatest effect on weight gain is observed in the first steps of impregnation: after the first 5 impregnations the weight gains were in the range between 12 and 13 wt%, due to the high initial pore volume of the samples (Table 1) while in the last five impregnations just 4–7 % weight gains were

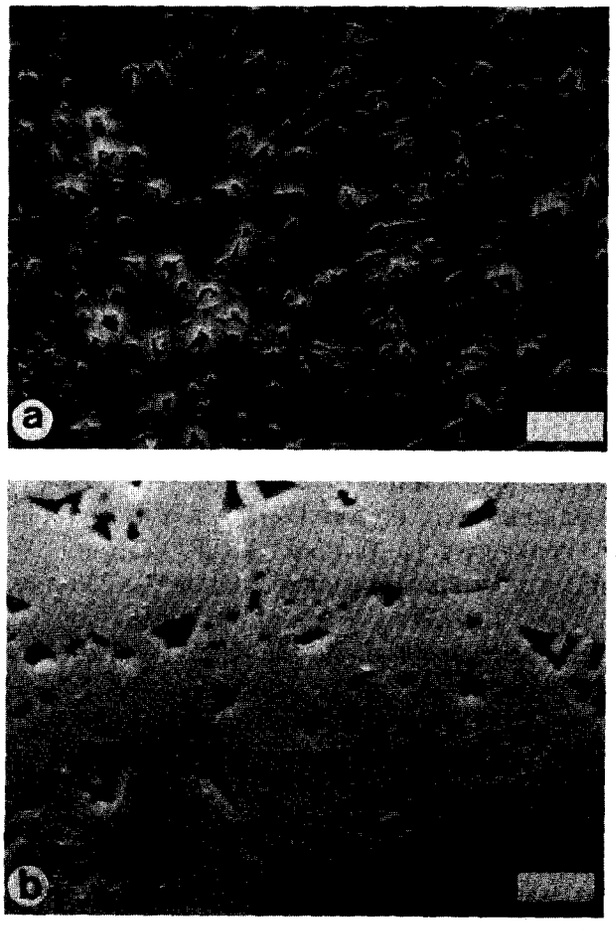

Fig. 1. SEM of polished and etched surfaces of fired Al_2O_3 (a) without and (b) with impregnation (bar: 10μm).

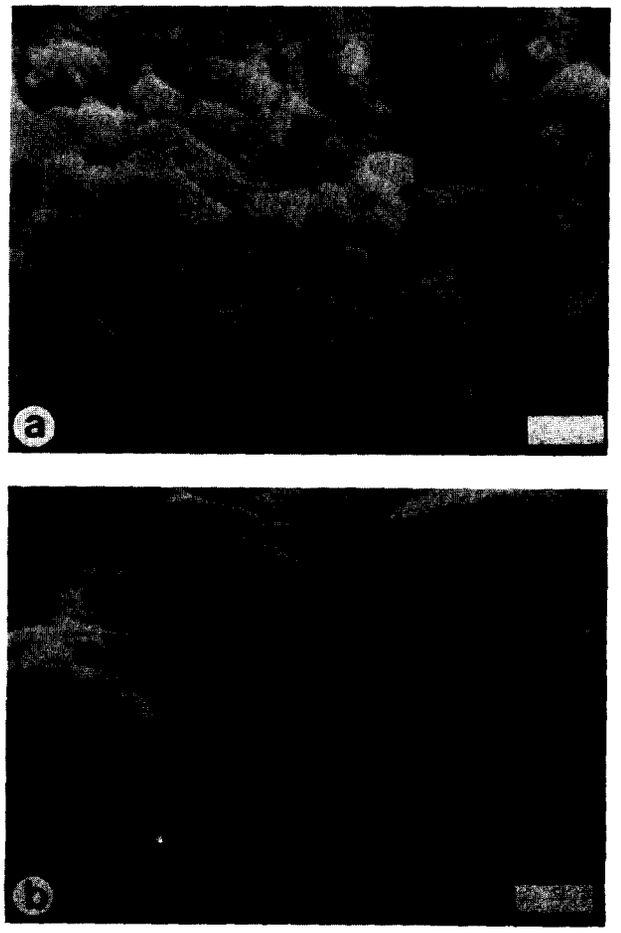

Fig. 2. SEM of fracture surfaces of fired Al_2O_3 with 10 vol% of SiC whiskers, (a) without and (b) with impregnation (bar: 10μm).

measured. The initial pore volume values for 0 and 5 vol% SiC_w show that the inhibiting effect of SiC_w on compaction is small for samples with 5 vol% whiskers. However, a noticeable increase in the initial pore volume for higher whisker contents (10 and 15 vol%) is observed, while the mean pore radius is between 40 and 50 nm for all the samples. After 15 impregnations, the final pore volume is almost the same in all the samples. This fact is in agreement with the higher weight gain measured in the samples with 10 and 15 vol% of whiskers and with the densities obtained (Table 2). Higher precalcined densities resulted from the precipitation of aluminium hydroxide into the pores followed by its thermal decomposition to aluminium oxide when the impregnation technique was used.

After firing, the improvement in densification behaviour caused by the impregnation is observed in the higher density values obtained for impregnated samples (Table 2). This fact is a consequence of both the higher precalcined density of the impregnated samples and the greater reactivity in sintering of the small particles incorporated during impregnation. The effect of the impregnation on the pore volume and grain growth is clearly observed in SEM photographs of polished surfaces of fired Al_2O_3 (Fig. 1). In the impregnated Al_2O_3 sample, less porosity is observed, since the pores were filled during the impregnation. Furthermore, the grain size in impregnated samples is 2–3 times higher than in non-impregnated ones. Also, the effects of the impregnation are shown in the SEM photographs of fracture surfaces of fired Al_2O_3 with 10 vol% whiskers without and with impregnation, respectively (Fig. 2).

It is well known that the densification of alumina depends on the nature of the sintering atmosphere. In this study, the density of the Al_2O_3 (3·70 g/cm^3) resulted lower than the density of the Al_2O_3 sintered in air (3·90 g/cm^3). This fact was attributed to the harmful effect on sintering behaviour of the highly reducing atmosphere present in the graphite resistance furnace at 1800°C. In these conditions, the partial pressure of oxygen, estimated from the Ellingham diagram (10^{-17}–10^{-20} atm), is so low that the alumina decomposition starts. So, other reactions occur[4] and the densification diminishes. However, the density obtained with impregnated Al_2O_3 (3·86 g/cm^3) was close to the value of the sample sintered in air. The impregnated samples containing whiskers also exhibited higher densities than the non-impregnated ones.

REFERENCES

1. SACKS, M. D., LEE, H. W. & ROJAS, O. E., Suspension processing of Al_2O_3/SiC whisker composites. *J. Am. Ceram. Soc.*, **71** (1988) 370–9.
2. BARCLAY, S. J., FOX, J. R. & BOWEN, H. K., Processing of pressureless-sintered SiC whisker-reinforced Al_2O_3 composites. *J. Mater. Sci.*, **22** (1987) 4403–6.
3. KIM, Y. W. & LEE, J. G., Pressureless sintering of Al_2O_3–SiC whisker composites. *J. Mater. Sci.*, **26** (1991) 1316–20.
4. URRETAVIZCAYA, G., CAVALIERI, A. L. & PORTO LÓPEZ, J. M., *Pressureless Sintering of Al_2O_3–SiC_w Composites*, Third Euro-Ceramics, Vol. 3, ed. P. Durán and J. F. Fernández, Faenza Editrice Ibérica S. L., Castellón de la Plana, Spain, 1993, pp. 683–8.