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Influence of Powder Drying Route on the Mechanical Properties of Alumina–Zirconia Composites

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Abstract

This paper compares Al_2O_3–ZrO_2 composites obtained from the same powder precursors dried by two different methods: spray drying and alcohol extraction via sol–gel route. The composite with 15% ZrO_2 obtained by sintering microsphere powders produced via a sol–gel method exhibited better mechanical properties.

In dieser Arbeit werden Al_2O_3–ZrO_2 Verbundwerkstoffe verglichen, die zwar aus den gleichen pulverförmigen Prekursoren hergestellt, aber in verschiedener Weise getrocknet wurden: Sprühtrocken und Alkoholextraktion nach dem Sol–Gel–Verfahren. Verbunde mit 15% ZrO_2 wurden durch Sintern mikrosphärischer Pulver hergestellt. Diese Werkstoffe zeigen bessere mechanische Eigenschaften für den Fall der Sol–Gel-Methode.

Ce travail traite des propriétés mécaniques des composites alumine–zircone obtenus par la voie sol–gel provenant de précurseurs minéraux halogénés mais séchés par des techniques différentes. Deux types de poudres de morphologie distincte ont été obtenues, des agglomérats par atomisation et des microsphères à partir d'une technique de séchage par voie alcoolique mise au point dans nos laboratoires. Les meilleures propriétés mécaniques ont été observées pour un dispersoïde fritté à partir des microsphères et contenant 15% en poids d'oxyde de zirconium ($\sigma_f = 760\ MPa$, $K_{IC} = 10\ MPa\sqrt{m}$, $H_V = 2300$).

1 Introduction

The control of microstructure and the understanding of strengthening mechanisms are necessary to produce a ceramic material with tailored physical and mechanical properties. Among other techniques, sol–gel processes are frequently employed to design appropriate microstructures.[1]

The purpose of this work is to compare Al_2O_3–ZrO_2 composites obtained by starting from the same gel and modifying the drying step for powder production: a spray-drying process is compared to a solvent extraction technique. These methods produced different primary particles whose organization gave rise to different microstructures, thus influencing the final mechanical properties.

2 Experimental Procedures and Results

2.1 Powder preparation

To produce alumina–zirconia (Al_2O_3–ZrO_2) composites containing 10, 15, 20 wt% ZrO_2, suitable quantities of $AlCl_3 . 6H_2O$ and $ZrCl_4$ were dissolved in distilled water. The hydroxides were precipitated at 25°C by adding 4N NH_4OH under continuous stirring. The final pH value of 9 was chosen by zeta-potential measurements. The gel was washed several times to remove chloride ions to the final content of 0·4 mol Cl^- per mol Al^{+3}. The gel was then divided into two parts: the first was dried at 300°C by spray-drying (SD); the second part was peptized by HCl in

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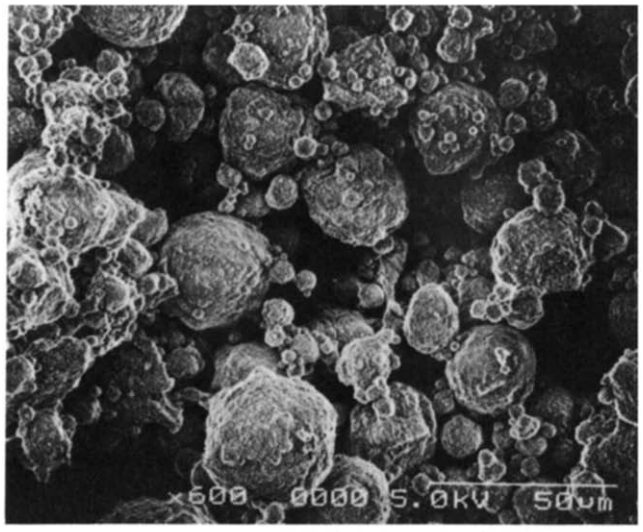
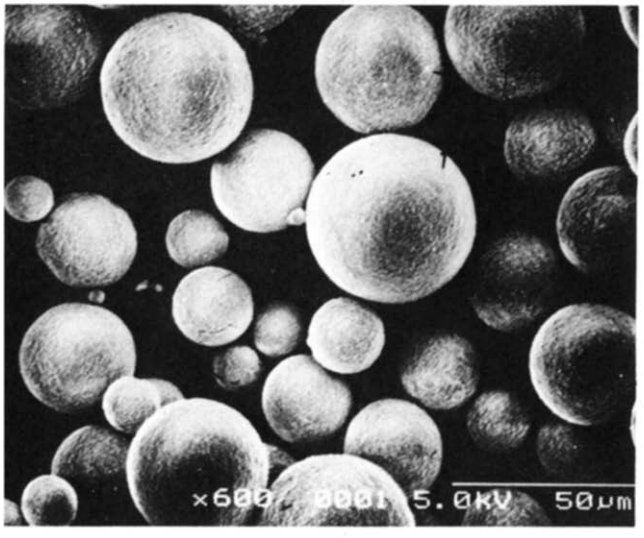




(b)

Fig. 1. Micrographs of (a) the SD and (b) the MS powders.

a sealed vessel at 80°C for 48 h. The resulting sol was concentrated down to 2M Al^{3+} by stirring it at 80°C. The sol was fed into a laboratory plant through a small nozzle and broken up to droplets which were slowly dehydrated by contact with 1-octanol and converted into solid gel microspheres which were drawn from the plant, dried at 300°C in an oven and labelled MS.[2]

The powders obtained by the SD process consisted of 15 μm spherical granules; those prepared by the sol–gel MS process were 25 μm average diameter microspheres. For both powders the ratio maximum diameter/average diameter of the particle size distribution was lower than 3, denoting a good size distribution. The micrographs in Fig. 1 show typical powders morphologies.

The BET surface areas of the SD and MS powders after thermal treatment at 300°C were 250 and 350 $m^2 g^{-1}$ respectively; after the heat treatment at 1200°C, areas of both powders decreased to 18–20 $m^2 g^{-1}$.

Table 1 Theoretical and experimental densities for each composition

Zirconia (wt%)	*Theoretical density ($g cm^{-3}$)*	*SD powders ($g cm^{-3}$)*	*MS powders ($g cm^{-3}$)*
10	4·13	3·88	4·09
15	4·21	3·92	4·16
20	4·29	3·99	4·28

XRD analysis of samples treated at different temperatures showed the presence of $Al(OH)_3$ (bayerite (traces) and gibbsite) at 300°C, tetragonal (t) ZrO_2 at 1100°C, and the presence of transition aluminas (mainly θ-Al_2O_3) at 1200°C, whereas α-Al_2O_3 could be observed only at 1300°C. The amount of α-Al_2O_3 was lower in MS powders compared with the equivalent SD samples treated at the same temperature, in agreement with previous observations.[3,4]

2.2 Sample sintering

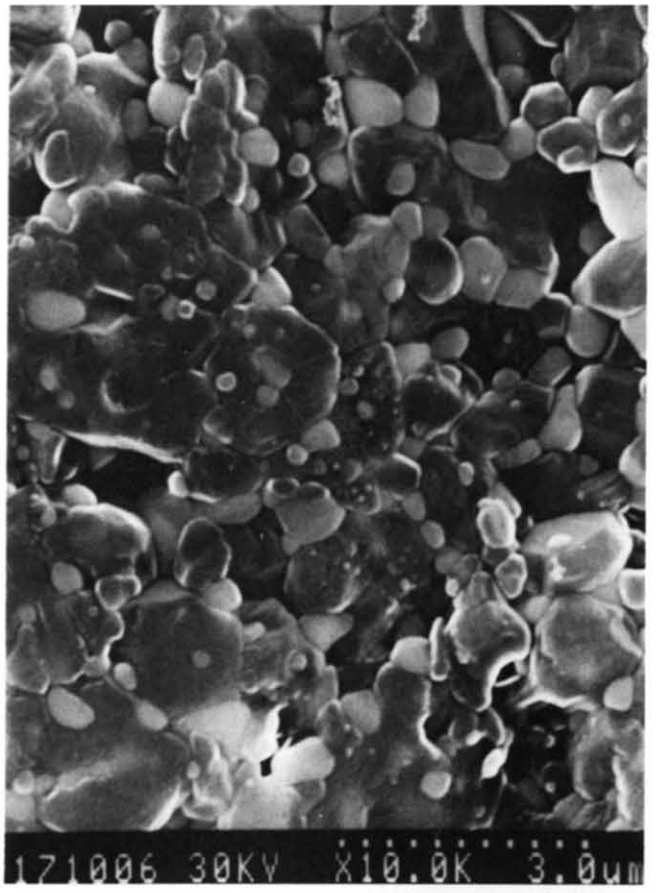
Powders were hot-pressed in a controlled atmosphere furnace under N_2 flow in a 35 mm diameter graphite die whose faces were covered with BN to avoid reaction with the powders to be sintered. Hot pressing was performed at 31 MPa at 1600°C for 30 min. Load was applied at 1450°C and kept constant throughout the firing cycle. The heating rate and cooling rate were 30°C min^{-1}. After hot-pressing, disks were machined to obtain parallel faces, cut into bars and polished before mechanical testing. Sample densities ($g cm^{-3}$) were measured by the water displacement method. The results for SD and MS powders are shown in Table 1.

3 Microstructures and Mechanical Properties

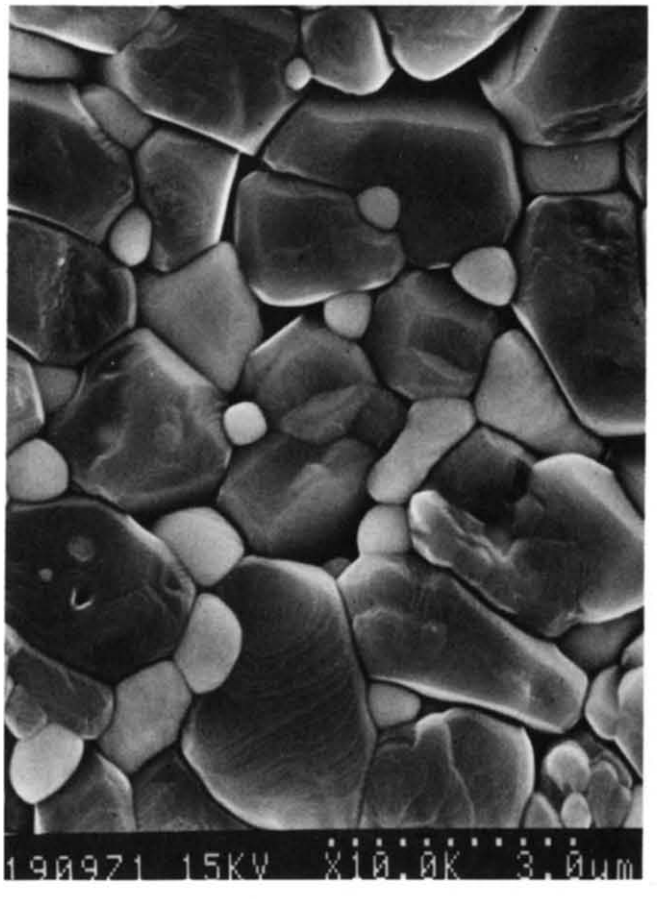
In both SD and MS samples, a homogeneous dispersion of ZrO_2 grains in the matrix could be observed. In SD samples some ZrO_2 grains could be found in intragranular positions, whereas in MS samples all ZrO_2 grains were in the intergranular positions. SEM images of samples thermally etched at 1500°C for 15 min revealed grain boundaries as presented in Fig. 2.

Flexural strength of the test bars (25 × 5 × 5 mm^3) was measured with a three-point bend test (points span was 19 mm) at room temperature. All tests were performed at a constant displacement rate of 0·2 mm min^{-1}. Highest values were found for samples containing 15 wt% ZrO_2 and MS samples always exhibited better strength values, as reported in Fig. 3.

Fracture toughness was evaluated by the single-edge notched-beam (SENB) method at room temperature with a controlled notch geometry



(a)



(b)

Fig. 2. Micrographs of the sintered products obtained from (a) the SD and (b) the MS powders.

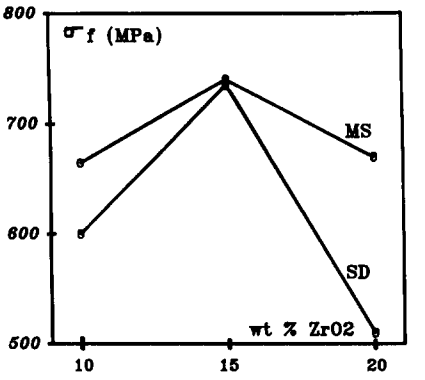


Fig. 3. Flexural strength of the composites obtained from the SD and MS powders.

(depth = 1 mm, thickness = 0·3 mm). Values are reported in Fig. 4.

Microhardness was measured by the Vickers indentation method with a load of 500 MPa (10 N) applied for 10 s and each value reported in Fig. 5 is the result of 10 indentation tests.

Grain size and t-ZrO_2 fraction were evaluated according to the procedure reported in the literature.[5,6] Samples containing 15 wt% ZrO_2 prepared with SD powders showed ZrO_2 and Al_2O_3 grain sizes to be, on average, 0·5 μm and 1·6 μm respectively, with a t-ZrO_2 content of 50%. On the other hand, samples containing 15 wt% ZrO_2 but sintered from MS powders, had average grain sizes of 0·8 μm for ZrO_2 and 1·5 μm for Al_2O_3 with a t-ZrO_2 content of 61%.

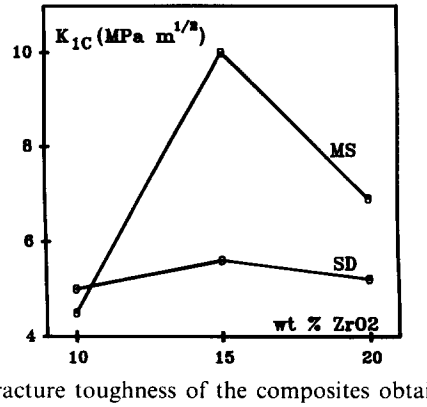


Fig. 4. Fracture toughness of the composites obtained from the SD and MS powders.

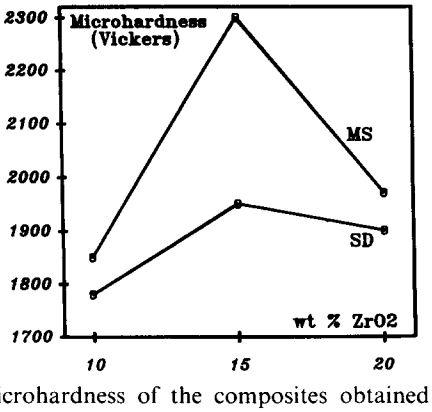
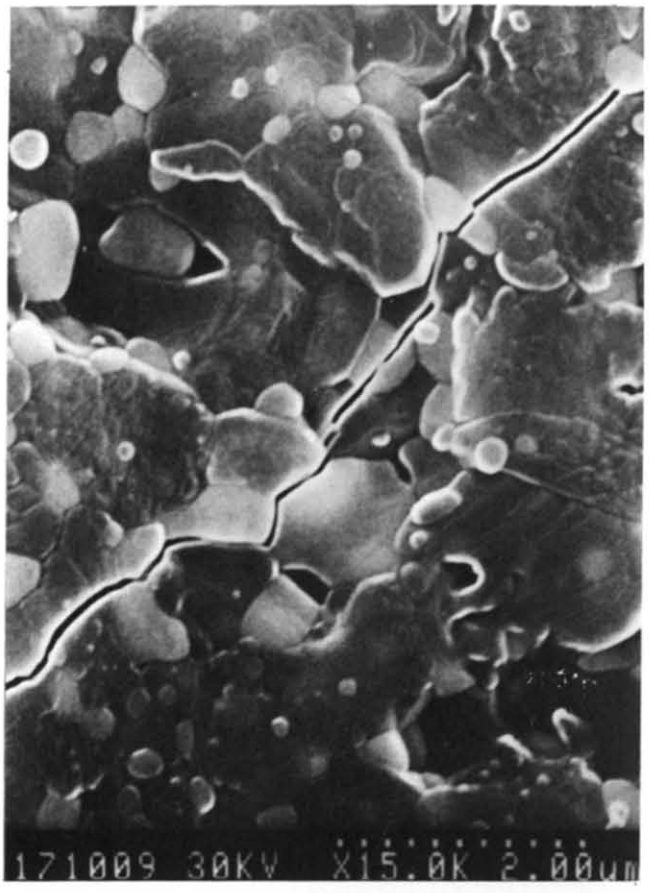
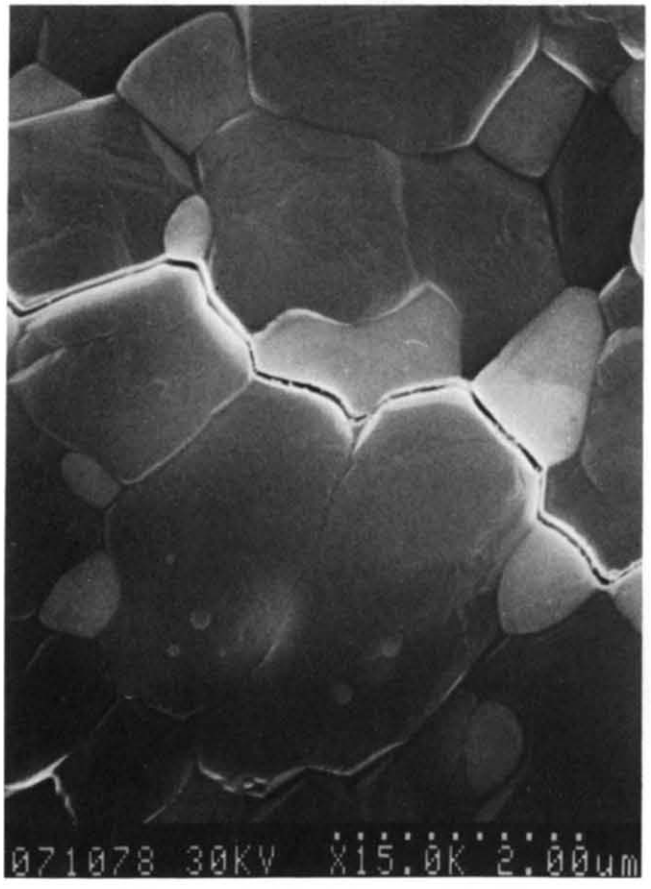


Fig. 5. Microhardness of the composites obtained from the SD and MS powders.



(a)



(b)

Fig. 6. Propagation of microcracks in the composites obtained from (a) the SD and (b) the MS powders.

To explain the higher value of K_{IC}, an indentation crack was made on the samples and the path of the microcrack in the composites observed. SEM images (Fig. 6) shows an intragranular fracture for composites obtained from SD powders, whereas the fracture is intergranular in the case of composites with MS powders.

4 Discussion

Strength (σ) and toughness (K_{IC}) figures herein reported compare fairly well with the published data for this type of composite material.[7-11] The best mechanical properties in the present investigation have been found in samples containing 15 wt% ZrO_2 (approx. 10·5 vol.%), whereas 15 vol.% ZrO_2 (approx. 21 wt%) was reported in the literature as the best performing composition obtained by attrition milling.[10,11]

The discrepancy with the literature data should be ascribed to the processing differences which, under the same nominal concentration, can produce very dissimilar particle size, distribution and t-/m-ZrO_2 ratio. In fact, the mechanical properties are a function of all these parameters and simplified one-to-one correlations cannot satisfactorily describe the material's behaviour.

5 Conclusion

The investigation showed that controlled pH gelation may produce Al_2O_3–ZrO_2 powder precursors with homogeneously distributed ZrO_2 particles, both via the spray-drying and the solvent-extraction techniques. Furthermore, it has been demonstrated that this latter type of drying produced powders (MS) that gave sintered materials with better strength, toughness and hardness. Among the tested compositions, samples with 15 wt% ZrO_2 performed best. The lack of a complete agreement with similar materials described in the literature, should depend upon the different powder processing routes and on the complexity of the microstructure–property relationships.

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