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Nanocoating of Al_2O_3 additive on ZrO_2 powder and its effect on the sintering behaviour in ZrO_2 ceramic

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Abstract ZrO_2 powder was coated with Al_2O_3 precursor generated by a polymeric precursor method in aqueous solution. The system of nanocoated particles formed a core shell-like structure in which the particle is the core and the nanocoating (additive) is the shell. A new approach is reported in order to control the superficial mass transport and the exaggerated grain growth during the sintering of zirconia powder. Transmission electron microscopy (TEM) observations clearly showed the formation of an alumina layer on the surface of the zirconia particles. This layer modifies the sintering process and retards the maximum shrinkage temperature of the pure zirconia.

Introduction

Nanostructured ceramics are of special interest to a wide range of applications as a result of their unique mechanical properties. Core-shell nanomaterials are recent addendums to nanoscience [1, 2].

Nanocoated particles are an entirely new class of materials, manifesting considerable potential for new applications. The combination of two materials on a nanometer scale, one acting as core and the other as coating, can result in interesting physical and chemical properties that are substantially different from those of the core, thus making them attractive from both a scientific and technological viewpoint [3, 4]. With an increasing number of different types of nanocoated particle and growing understanding of the resulting properties owing to the small particles that are embedded in a second phase, new and interesting applications should become available [5, 6].

The main applications of these new nanocoated particles may either be seen in the formation of diffusion barriers to avoid grain growth or in the modification of physical properties of the core and the chemical properties of the surface [6].

Nanocoated ceramic particles can be obtained if the phase diagram exhibits low or no mutual solubility. This is an important condition to obtain coated nanoparticles. Special interest is currently being granted to ZrO_2–Al_2O_3 system because the components are hard to dissolve one into the other in a solid solution. This is favourable to inhibit grain growth primarily by interdiffusion of atoms along the relevant grain and interphase boundaries in a controlled composite microstructure [7].

The present paper is focused on the sintering behaviour of a new type of nanostructured ceramics made from zirconia powder grain coated with alumina.

Sintering is the process whereby interparticle pores in a granular material are eliminated by atomic diffusion driven by capillary forces. The observation made by Coble [8], that certain crystalline granular

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solids could gain full density and translucency by solid-state sintering, was an important milestone for modern technical ceramics. But these final-stage sintering processes are accompanied by rapid grain growth [9], because the capillary driving forces for sintering (involving surfaces) and grain growth (involving grain boundaries) are comparable in magnitude, both being proportional to the reciprocal grain size.

In order to fabricate dense specimen with nanosized grains, in general, one of the methods used is to incorporate second-phase dispersoids to matrix. The grain boundary pinning effect of the second phase particles can suppress coarsening of grains [10].

This work is based on the control of material diffusion mechanisms by means of a small amount of additive. As it is desirable that this additive acts preferentially on the grain surface we propose application of a nanocoating of the additive (Al_2O_3) over the particle to be sintered (ZrO_2).

Experimental procedure

Processing

The start materials were aluminium nitrate, (Aldrich, purity >99.9%) and high purity *m*-ZrO_2 nanopowder (Tosoh grade TZ-O, purity >99.9%), citric acid (E. Merck, purity >99.9%) and ethylene glycol (Mallinckrodt Baker).

The ZrO_2 powder was dispersed in water using an ultra-sonic probe. An Al polymeric precursor water-based solution was used to coat the ZrO_2 nanocrystals. The aluminium citrate aqueous solution was prepared from aluminium nitrate and citric acid. Ethylene glycol was added to the citric acid to promote a polymerization reaction.

This Al solution was added to the ZrO_2 suspension and then the solvent was evaporated at 70 °C with rotary evaporator. The dried material was decomposed for 4 h at 350 °C to remove the organic waste. Thereafter, the samples were compacted using uniaxial and isostatic pressing to obtain cylindrical samples, having a diameter of 9 mm.

The green pellets were then sintered in a dilatometer with a heating rate of 10 °C min^{-1} up to 1550 °C (Netsch, model 402E, Germany) in air atmosphere.

Characterization

Phase identification was carried out by X-ray diffraction (XRD) analysis (D5000, Siemens, Germany) using CuKα radiation. The coated ZrO_2 powders were observed with the use of a transmission electron microscope (TEM). These observations were performed on a JEOL 3010 ARP microscope operating at an acceleration voltage of 300 kV.

The crystallite size of the powders was determined using the Scherrer equation:

$$D_{\mathrm{hkl}} = K\frac{\lambda}{\beta\cos\theta} \tag{1}$$

where λ is the wavelength (CuK_1), θ the diffraction angle, K a constant, and β the corrected half-width of the diffraction peak. The diffraction peak profile was fitted using a pseudovoigth function to calculate the full width at half maximum (FWHM). Only CuK_1 radiation was considered; CuK_2 radiation was subtracted via computer program software (FIT Program, Diffract AT, Siemens, Germany). The β value was determined considering the following equation:

$$\beta = (B_{\mathrm{obs}}^2 - b^2)^{1/2} \tag{2}$$

where B_{obs} is the FWHM that is related to the sample and b is the FWHM of the external standard [quartz (SiO_2)].

Surface area measurements of the different samples were determined by analysis of nitrogen adsorption/desorption isotherms, which were obtained at liquid nitrogen temperature using a Micrometrics ASAP 2400 system.

Results and discussion

The samples were characterized by TEM in the initial stage of the sintering process in order to understand the effect of nanocoating on the sintering process.

Porous sintered samples are difficult to prepare for TEM analysis. Moreover, the ion-thinning process, normally used to prepare such samples, may introduce artifacts, especially for grain boundary analysis [11]. To overcome this problem, a methodology similar to that developed by Chiang and coworkers [12] was used, preparing a noncompacted sample and heat-treating this powder to critical temperatures that were selected based on a dilatometric study.

By totally eliminating the organic material there is a formation of an amorphous nanocapsule, which can be confirmed by the TEM images of the coated ZrO_2 powder (named $ZrO_2@Al_2O_3$) heat treated at 1080 °C (Fig. 1). Such micrographs reveal almost spherical particles, which consist of a core of zirconia surrounded by a coating of alumina. The core is crystalline, whereas the coating is amorphous.

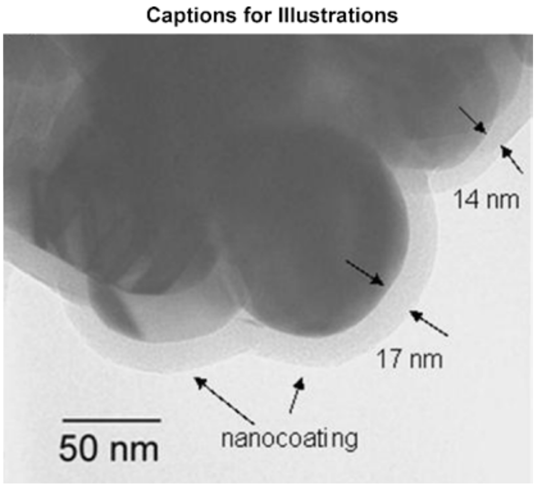

Fig. 1 TEM images of $ZrO_2@Al_2O_3$ powder heat treated at 1080 °C for 5 min

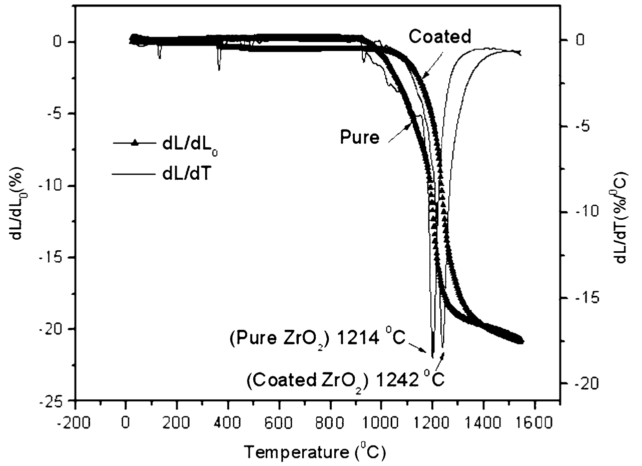

Fig. 3 Dependence of the relative shrinkage on sintering temperature of the pure ZrO_2 and $ZrO_2@Al_2O_3$ pellets

The core sizes range from 50 to 100 nm. The thickness of the amorphous coating is at a range that goes from 14 to 17 nm (Fig. 1).

The centre of these particles is darker than their outer regions. This is because of the weaker absorption of the electrons in the amorphous alumina layer when compared with the zirconia kernel (difference in atomic number between aluminium and zirconium). Similarly, Vollath et al. [6] observed amorphous coatings on ZrO_2 particles prepared by microwave plasma processing.

Figure 2 presents X-ray diffractograms of the pure and coated ZrO_2 pellets after sintering. In this stage the Al_2O_3 capsule is no longer amorphous. The XRD patterns of these samples clearly show the presence of crystalline *m*-ZrO_2 (monoclinic phases). As can be more advantageously seen in the diffractogram related to the powder containing 2.5 mol% Al_2O_3 and heat treated at 1500 °C, the capsule crystallizes as α-alumina, considering that this additive had not dissolved in zirconia matrix.

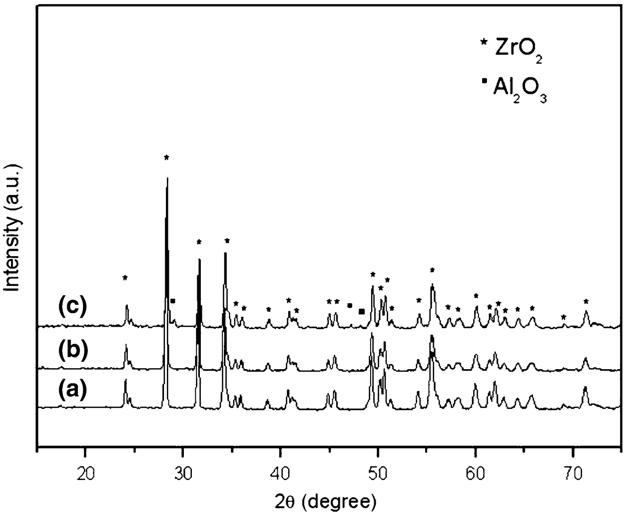

Fig. 2 X-ray diffraction patterns for the sintered pellets, heat treated at 1500 °C (**a**) pure ZrO_2; (**b**) 1 mol% Al_2O_3 coated ZrO_2; (**c**) 2.5 mol% Al_2O_3 coated ZrO_2

The dynamic sintering and the derivatives of the linear shrinkage curves up to 1550 °C of uncoated and coated ZrO_2 are represented in Fig. 3. As can be observed the uncoated ZrO_2 sample starts to display linear shrinkage at temperatures above 950 °C, whereas coated ZrO_2 sample begins to shrink at 1080 °C. However, both curves display strong linear shrinkage indicating intense mass transport.

The derivative of the linear shrinkage curve for the uncoated sample reaches a maximum at 1214 °C (Fig. 3). A small increase in the maximum differential shrinkage temperature of the coated sample was observed, reaching 1242 °C. Subsequently, the alumina considerably retards the sintering of the coated zirconia owing to low mobility through the alumina phase segregated at the grain growth boundaries. Therefore, it is obvious to assume that the Al_2O_3 additive changes the sintering behaviour of the ZrO_2 powder. Similar behaviour was observed by Srdic et al. [13].

The Al_2O_3 coating also proved to effectively inhibit grain growth at low temperatures, decreasing the grain growth rate or, more specifically, the crystallite growth rate (determined by the Scherrer equation) by as illustrated in Fig. 4. As can be seen, the $Al_2O_3@ZrO_2$ powder exhibited a satisfactory stability against grain growth up to 1200 °C, while the pure ZrO_2 showed intense grain growth, particularly at temperatures

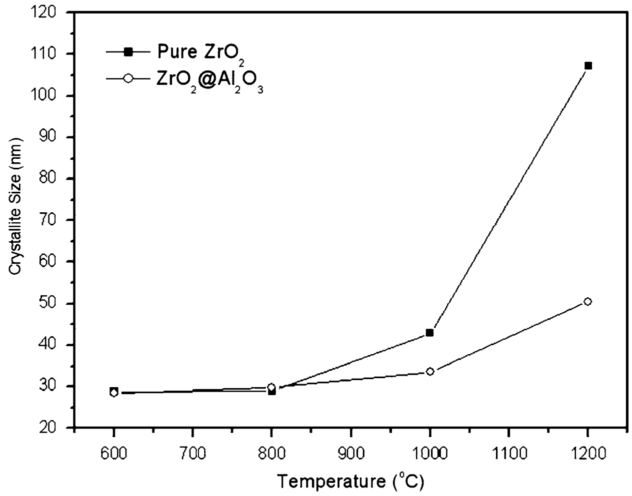

Fig. 4 Dependence of the crystallite size on the sintering temperature for pure and coated ZrO$_2$ powder

Table 1 Surface area values of the coated and uncoated ZrO$_2$ as function of the heat treatment

Temperature (°C)	Specific surface area (m^2 g^{-1}) pure ZrO$_2$	Specific surface area (m^2 g^{-1}) coated Al$_2$O$_3$
600	13.38	16.57
800	13.37	15.41
1000	7.65	11.01
1200	1.82	6.33

exceeding 1000 °C. Here, a great number of the particles have been considered. Therefore, a discrepancy it is acceptable between the particle size determined by the Scherrer equation (Fig. 4) and particle size estimated by using TEM technique (Fig. 1) in which punctual values were considered.

Table 1 designates the variation of the surface area of coated and uncoated zirconia as a function of the heat treatment. In both cases the surface area were found to be decreased with temperature increase, however, the values observed for the coated materials are predominantly higher than for the uncoated materials. These results corroborate observation based on the data deriving from studies of crystallites sizes, which presents finer particles in Al$_2$O$_3$@ZrO$_2$ than in pure ZrO$_2$, most likely due to the effective role of Al$_2$O$_3$ additive as a grain growth inhibitor for the matrix grains.

Conclusions

It has been demonstrated that the polymeric precursor method can be successfully used in obtaining nanocapsules on the surface of crystallines oxides.

The different coated powder characteristics display changes in sinterability when compared with pure zirconia.

Zirconia coated with alumina exhibits considerable reduction in grain growth and retards the sintering. These results suggest that alumina segregates at the interfaces between the ceramic grains during the sintering process. The coating acting as a diffusion barrier inhibits grain growth. This behaviour is essential when physical properties depend strongly on the size of the particles. The nanocoating based on core-shell structures offers great potential for new applications.

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