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Preparation and pressureless sintering of nanostructured zirconia–titania composite powders

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TiO_2 doped yttria–zirconia nanosized powders were prepared by the coprecipitation method, with particle sizes of 10–15 nm. The effects of TiO_2 content and calcining temperature on the phase structure and grain size of powders were studied. Nanopowders were compacted uniaxially and densified in a muffle furnace. Densification studies show that the dense pellet of yttria stabilized tetragonal zirconia polycrystal (Y-TZP)–TiO_2 is obtained after sintering at 1200 °C. The presence of TiO_2 inhibits grain growth and suppresses the densification process of pure Y-TZP. Ceramics with a mean grain size of 39 nm can be obtained based on the powder that has been doped with 30 mol % TiO_2.

Key words: *ZrO_2–Y_2O_3–TiO_2; crystallization; nanocomposites; pressureless sintering*

1. Introduction

Nanostructured materials, characterized by an ultrafine grain size, have stimulated much research interest by virtue of their unusual mechanical, electrical, optical, and magnetic properties. Nanocrystalline ceramics, in which grain sizes smaller than 100 nm occur, are believed to have special characteristics, such as superplasticity at low temperature [1–4]. However, fabrication of a dense bulk nanocrystalline ceramics is very challenging, since an inevitable grain growth occurs at relatively high sintering temperatures needed for densification. Nanocomposites constructed by dispersing second-phase nanosize particles within the matrix grains and on the grain boundaries, lead to a new concept of material design which significantly improves strength and also provides moderate enhancement in fracture toughness [5]. On the other hand, the nano/nano-type composites which were composed of the dispersoids and matrix grains (both of nanometer size) showed additionally attractive properties, due to a peculiar

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role of nanosized phases in physical and mechanical properties [5, 6]. Therefore, nanocomposites have been the subject of intensive research in recent years.

ZrO_2–Y_2O_3 systems find a wide variety of applications in many advanced structural, high-temperature and electrical applications due to their unique properties such as high hardness, low wear resistance, low coefficient of friction, high elastic modulus, chemical inertness, low thermal conductivity, high fracture toughness and high melting point [7, 8]. Nevertheless, their mechanical properties at room temperature do not deliver guaranteed results. It is well known that the strength of yttria stabilized tetragonal zirconia polycrystal (Y-TZP) may decrease drastically during ageing in air at temperatures between 100 °C and 400 °C [9–11]. At these temperatures, the tetragonal–monoclinic (t–m) phase transformation is activated by the environment, and the volume expansion that takes place can generate microcracks in the transformed surface, thereby degrading the strength and surface properties of the material. It has been reported that the uniform distribution of Al_2O_3 to ZrO_2 matrix can suppress the low-temperature degradation of mechanical properties. In addition, a dopant can control the microstructure by a prevention of the abnormal grain growth and refinement of matrix grains [12–14]. Thus it seemed interesting to prepare Y_2O_3 doped ZrO_2 (Y-ZrO_2) based mixed oxides and to study their structural and morphological behaviour. Similar materials are also of interest in the field of the preparation of Y-TZP based ceramics as engineering materials.

In earlier studies, ZrO_2–Y_2O_3–Al_2O_3 and ZrO_2–Y_2O_3–CuO nanocrystalline powders were prepared using the chemical coprecipitation method. On this basis, Y-TZP/Al_2O_3 and Y-TZP/CuO nanoceramics were prepared successfully by the authors [15–18] by pressureless sintering. Tetravalent dopants such as Si^{4+}, Ce^{4+} etc., were also found to be effective agents to stabilize t-ZrO_2 forming cationic networks and high-energy surface layers [19, 20]. In the zirconia-rich end of the titania phase equilibrium diagram, TiO_2 is known to dissolve into tetragonal ZrO_2 up to 18 mol % at high temperatures and act as a stabilizing agent in a manner similar to Y_2O_3 and CeO_2 [21]. Therefore, ZrO_2–Y_2O_3–TiO_2 could be an interesting challenge. In this work, ZrO_2–Y_2O_3–TiO_2 nanosized powders with various TiO_2 contents were synthesized by chemical coprecipitation. The sintering behaviour and microstructure of the bulk ceramics prepared by pressureless sintering was investigated.

2. Experimental

Homogeneous 3Y-ZrO_2 and TiO_2 powder mixtures with nanosized particles were synthesized by coprecipitation [15, 16]. $ZrOCl_2{\cdot}8H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ and $TiCl_4$, selected as starting materials, were dissolved in deionized water to prepare a transparent metal salt solution with TiO_2 content from 5 mol % to 30 mol% relative to 3Y-ZrO_2. $NH_3{\cdot}H_2O$ solution was prepared separately with deionized water. The two solutions were then mixed and continuously stirred to obtain a homogenous solution, and the pH of the solution was adjusted to 9–10 by adding ammonia. The precipitate was filtered

and washed repeatedly with deionized water to remove NO_3^- and Cl^- anions and then washed with ethanol for three times. Then the precipitates were dried in an oven for 24 h and calcined at various temperatures for 2 h. The product was ground in an agate mortar, and nanosized powders were obtained. The products were referred to as ZT05, ZT10, ZT15 and ZT30 for 3Y-ZrO_2–TiO_2 binary oxide samples with TiO_2 contents from 5 mol % to 30 mol% relative to 3Y-ZrO_2. X-ray powder diffraction (XRD) for the powders was recorded on a D/max-RB diffractometer using CuK_α radiation (λ = 0.15406 nm). The EDS analysis of powders was performed on a scanning electron microscope (SEM, JEOL JSM-5600LV). The grain size was estimated from the full width at half maximum (FWHM) by the Scherrer equation and confirmed by a transmission electron microscope (TEM, JEM1200EX).

The green compact pellets were obtained by uniaxial pressing of the 3Y-ZrO_2 and 3Y-ZrO_2–TiO_2 powders at 1000 MPa for 5 min in air at room temperature. The nanocomposites were prepared by heating the green compacts in air at the rate of 5 °C/min up to a predetermined temperature and sintering for 4 h at that temperature. Archimedes' principle was used to measure the bulk density. XRD (D/max-RB) was used to deduce the crystalline phases and grain size of the sintered samples. The fracture surfaces of the sintered pellets were examined by scanning electron microscopy (SEM, JEOL JSM-6701F).

3. Results and discussion

3.1. Morphological properties and phase structure of the powders

The XRD patterns of 3Y-ZrO_2, and four mixed oxides with various TiO_2 contents after calcination at 600 °C are shown in Fig. 1. It is seen that the ZT30 and ZT15 after calcination at 600 °C were in an amorphous form. For the ZT10, the XRD shows a line at 30° corresponding to tetragonal ZrO_2. Although the XRD patterns of ZT10 have a feature line of tetragonal ZrO_2, the sample exhibits mostly the characteristics of amorphous phase. Relatively speaking, the ZT05 exhibits stronger tetragonal phase structure.

Figure 2 shows the XRD patterns of binary oxide samples after calcination at 800 °C. One can see that the XRD patterns of the five mixed oxides show the strongest diffraction peak of t-ZrO_2 phase. The 3Y-ZrO_2, ZT05 and ZT10 samples also show other diffraction peaks corresponding to the monoclinic phase structure, except for the ZT15 and ZT30 samples with a single t-ZrO_2 phase. The inset in Fig. 2 represents the relationship between TiO_2 content and phase composition. The volume fraction of the monoclinic phase (V_m) was determined by the empirical formula [22]:

$$V_m = \frac{[I_m(111) + I_m(11\bar{1})]}{[I_m(111) + I_m(11\bar{1}) + I_t(111)]}$$

where I_m denotes the intensities of the monoclinic peaks, and I_t denotes the intensities of the tetragonal peaks.

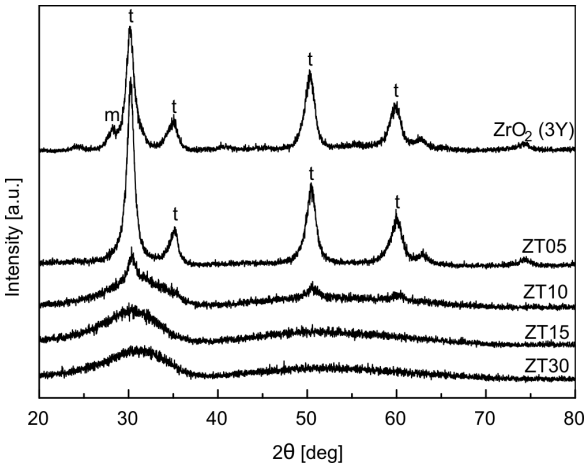

Fig. 1. XRD patterns of 3Y-ZrO_2 and 3Y-ZrO_2–TiO_2; t – tetragonal, m – monoclinic

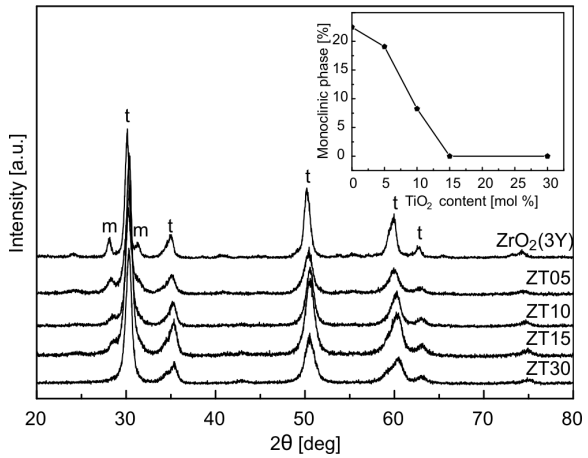

Fig. 2. XRD patterns of 3Y-ZrO_2 and 3Y-ZrO_2–TiO_2 powders calcined at 800 °C; t – tetragonal, m – monoclinic. The inset represents the relationship between TiO_2 content and phase composition

It can be seen that the phase composition follows a decreasing trend in monocline volume fraction as TiO_2 content increases. The monocline volume fraction of ZT05 powders is 19.1 vol. %. In the ZT10 sample, the monocline content decreases to 8.3 vol. %. The peak of monoclinic phase disappeared when the TiO_2 content increased further. It seems that the addition of TiO_2 delayed the phase transformation of zirconia from the tetragonal metastable phase to thermally stable monoclinic phase at 800 °C.

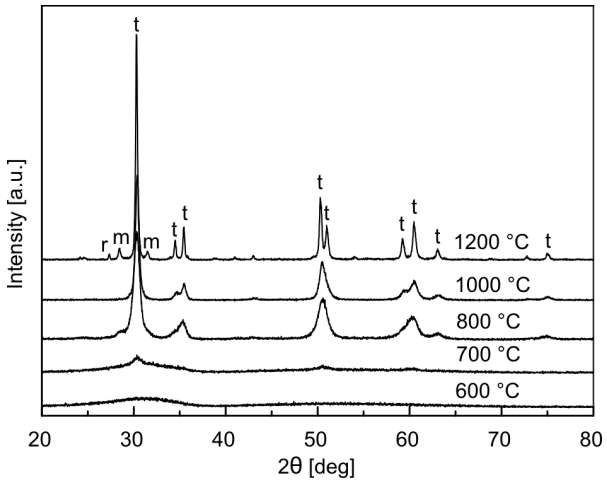

Fig. 3. XRD patterns of ZT15 powders calcined at various temperatures; t – tetragonal, m – monoclinic, r – rutile

The crystallization process with increasing temperature for the dried 3Y-ZrO_2 powder with 15 mol % TiO_2 was studied by the XRD technique, as shown in Fig. 3. It indicates that the dried gel existed as a totally amorphous mixture, and heating at temperatures lower than 700 °C did not cause any crystallization of the gels. Above 700 °C, there appeared crystallization peaks of the tetragonal ZrO_2 phase. The t-ZrO_2 peaks, with large full widths at the half maximum, indicate that the average crystallite size was small. With increasing temperature, the higher intensity and much sharper ZrO_2 peaks were observed. The XRD pattern after calcination at 1000 °C shows only t-ZrO_2. But rutile-TiO_2 and m-ZrO_2 were found to appear at 1200 °C.

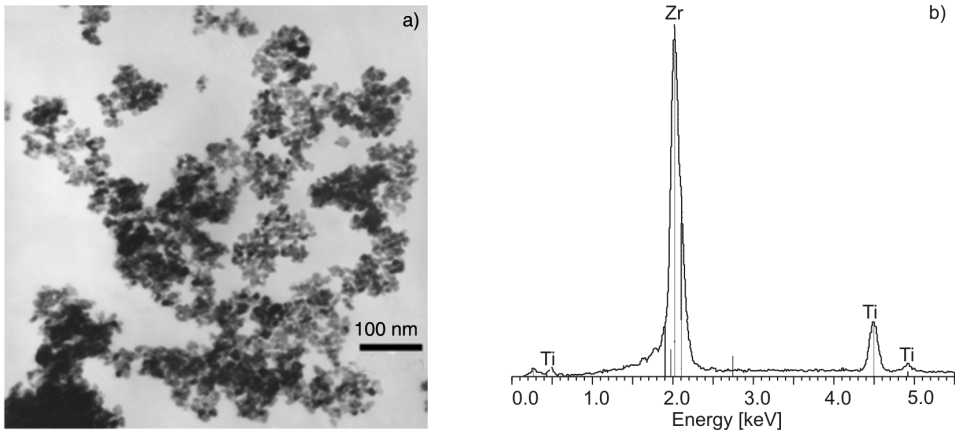

Fig. 4. TEM image (a) and EDX spectrum (b) of the ZT15 powder after calcination at 800 °C

Figure 4 shows the TEM photograph and EDS profile for ZT15 powders after calcination at 800 °C. It is seen that the agglomerates in Fig. 4a consist of almost spheri-

cal primary crystalline particles with the sizes of 10–15 nm. The EDS analysis exhibited clear peaks of Zr and Ti from any detected site. These results indicate that the homogeneous nanosized composite powder could be obtained by this coprecipitation process.

3.2. Sintering behaviour and microstructures

Figure 5 shows relative densities of specimens of various compositions in function of sintering temperatures. It can be seen that the presence of TiO_2 suppresses the densification process of Y-TZP. In samples without addition of TiO_2, densification starts at 600 °C and increases continuously [17, 18].

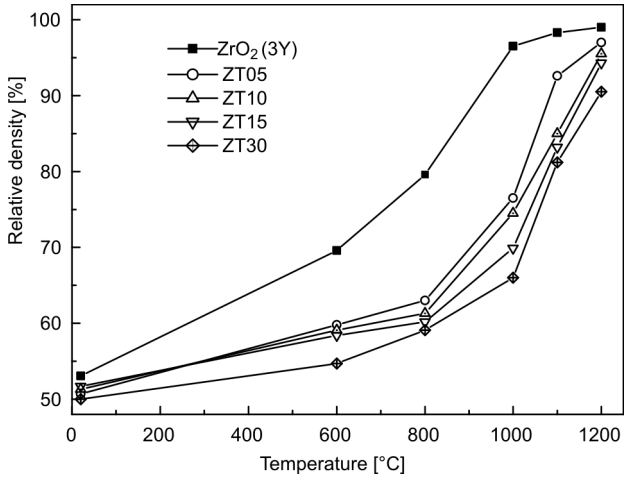

Fig. 5. Relative density in function of the sintering temperature

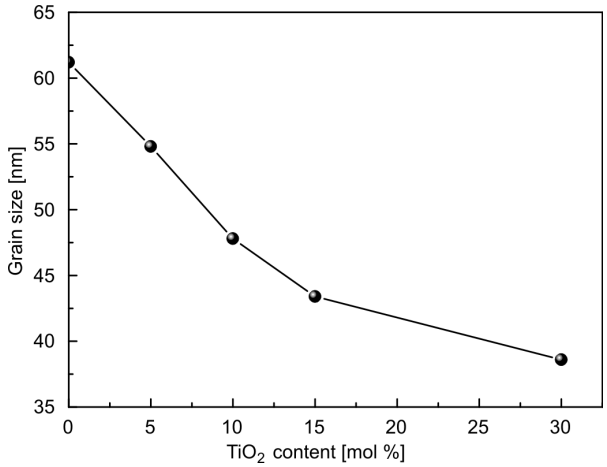

Fig. 6. Effect of TiO_2 content on the grain size of Y–TZP–TiO_2 sintered at 1200 °C

The powder doped with TiO_2 exhibits a lower sintered density at the same temperature. Note that, after sintering at 600 °C, low densities (about 60%) are obtained for the samples doped with TiO_2, but all 3Y-ZrO_2–TiO_2 oxides can be densified above 90% at 1200 °C. Effect of TiO_2 content on the grain size of Y-TZP sintered at 1200 °C is presented in Fig. 6. Grain size was calculated from X-ray line broadening. Obviously, the presence of TiO_2 inhibits grain growth dramatically. The powder that has been doped with 30 mol % TiO_2 and sintered at 1200 °C has a very small grain size (only 39 nm): the SEM micrograph of this specimen is shown in Fig. 7. Some uniaxial grains and polyhedral morphology are found in the SEM micrograph. The grains have a primary diameter of about 50–100 nm, which is larger than that determined from the corresponding X-ray peak broadening. The grains in the SEM photograph could be agglomerates comprised of several individual grains [18].

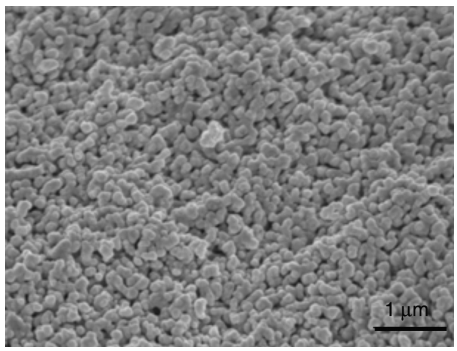

Fig. 7. SEM fractograph of Y-TZP/30mol %TiO_2 sintered at 1200 °C

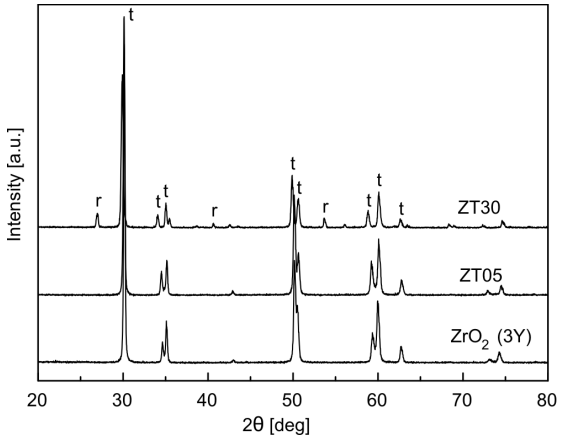

Fig. 8. The XRD patterns of the zirconia based nanocomposites sintered at 1200 °C; t – tetragonal, r – rutile

Evolutions of phases were investigated in function of sintering temperature, using X-ray diffraction. The phase composition of the Y-TZP/TiO_2 nanocomposites re-

mains almost unchanged after sintering at temperatures up to 1200 °C (see Fig. 8). The XRD patterns of the three samples show the strongest diffraction peak of t-ZrO_2 phase. The sintered sample doped with 30 mol % TiO_2 also showed the other diffraction peaks for the rutile phase structure.

4. Conclusions

Homogeneous 3Y-ZrO_2–TiO_2 nanosized particles can be obtained by a coprecipitation process. The presence of TiO_2 inhibits grain growth and suppresses the densification process. The dense zirconia based nanocomposites with a fine grained microstructure can be pressurelessly sintered in air using a powder prepared by coprecipitation. The sintered bodies (1200 °C) of doped TiO_2 (30 mol %) were composed mainly of tetragonal and a small amount of rutile phase, with a very small grain size (only 39 nm) calculated by X-ray line broadening.

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