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Journal of the European Ceramic Society 26 (2006) 3607–3612

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Yb_2O_3 and Y_2O_3 co-doped zirconia ceramics

Yanmei Kan[a], Guojun Zhang[a], Peiling Wang[a], Omer Van der Biest[b], Jef Vleugels[b,*]

[a] *State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 200050 Shanghai, PR China*

[b] *Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium*

Received 10 August 2005; received in revised form 2 January 2006; accepted 13 January 2006

Abstract

A suspension stabilizer-coating technique was employed to prepare x mol% Yb_2O_3 (x = 1.0, 2.0, 3.0 and 4.0) and 1.0 mol% Y_2O_3 co-doped ZrO_2 powder. A systematic study was conducted on the sintering behaviour, phase assemblage, microstructural development and mechanical properties of Yb_2O_3 and Y_2O_3 co-doped zirconia ceramics. Fully dense ZrO_2 ceramics were obtained by means of pressureless sintering in air for 1 h at 1450 °C. The phase composition of the ceramics could be controlled by tuning the Yb_2O_3 content and the sintering parameters. Polycrystalline tetragonal ZrO_2 (TZP) and fully stabilised cubic ZrO_2 (FSZ) were achieved in the 1.0 mol% Y_2O_3 stabilised ceramic, co-doped with 1.0 mol% Yb_2O_3 and 4.0 mol% Yb_2O_3, respectively. The amount of stabilizer needed to form cubic ZrO_2 phase in the Yb_2O_3 and Y_2O_3 co-doped ZrO_2 ceramics was lower than that of single phase Y_2O_3-doped materials. The indentation fracture toughness could be tailored up to 8.5 MPa m$^{1/2}$ in combination with a hardness of 12 GPa by sintering a 1.0 mol% Yb_2O_3 and 1.0 mol% Y_2O_3 ceramic at 1450 °C for 1 h.

Keywords: ZrO_2; Mechanical properties; Microstructure-final; Sintering; Electron microscopy; Yb_2O_3; Y_2O_3

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1. Introduction

Zirconia is an attractive candidate not only as a structural material because of its high toughness and strength,[1–3] but also as an electrolyte in solid oxide fuel cells (SOFCs) due to its excellent oxygen ion conductivity and stability in both oxidizing and reducing atmospheres.[4–6] Pure zirconia has three polymorphs: monoclinic (*m*), tetragonal (*t*) and cubic (*c*). The transformation between different polymorphs is very important for the processing and mechanical properties of zirconia ceramics. The $t \rightarrow m$ transformation in pure zirconia during cooling is accompanied by a volume change of 4–5%, which leads to crumbling of sintered pieces. In order to obtain stable *t*- or *c*-phase zirconia at room temperature, many studies have been focused on doped zirconia with aliovalent and rare earth oxides, such as CaO, MgO, Y_2O_3 and CeO_2.[2,7]

Over the last 20 years, most of the published literature reports zirconia ceramics doped with a single oxide. Although optimised properties can be obtained in these ceramics, a relatively large amount of dopant is needed. For example, good mechanical properties are often achieved in 3Y-TZP,[2] and for the use as an electrolyte in SOFCs, more than 8 mol% Y_2O_3 has to be added to get *c*-ZrO_2 with high oxygen ion conductivity.[8] Recently, Xu et al. found that stabilized ZrO_2 (TZP) ceramics could be obtained by co-doping with small amounts of Nd_2O_3 and Y_2O_3 (<3 mol%) and the material exhibited excellent mechanical properties.[9] It is reported that the phase stability of single oxide doped zirconia shows a strong dependence on the size of the rare earth cation, being optimal for Yb and Y, and declining for both larger and smaller cations.[10] Therefore, it can be expected that stable *t*- or *c*-ZrO_2 ceramics could be fabricated with a smaller amount of stabilizer by introducing Yb_2O_3 and Y_2O_3 simultaneously in ZrO_2.

The route for preparing starting powders has a strong influence on the properties of sintered ZrO_2 ceramics. The most common way for producing Y_2O_3-doped ZrO_2 powder is co-precipitation. High toughness can be achieved in co-precipitated ZrO_2 ceramics via optimisation of the sintering parameters or by post-sintering heat treatment at higher temperature for a long time.[11,12] In recent years, the stabiliser-coating technique has become more attractive, because Y_2O_3-stabilized ZrO_2 ceramics derived from Y_2O_3-coated starting powders

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[*] Corresponding author. Tel.: +32 16 321244; fax: +32 16 321992.
E-mail address: jozef.vleugels@mtm.kuleuven.be (J. Vleugels).

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doi:10.1016/j.jeurceramsoc.2006.01.007

show better mechanical properties than those fabricated from co-precipitated powders.[7,13,14] In the present study, Yb_2O_3 was chosen as the secondary stabilizer to explore the fabrication of Yb_2O_3 and Y_2O_3 co-doped ZrO_2 ceramics. A stabiliser-coating route was employed to prepare the starting powders. The sintering behaviour, mechanical properties, microstructure and phase assemblage were investigated.

2. Experimental procedure

Yb_2O_3 and Y_2O_3 co-doped ZrO_2 powders with an overall composition of $x\mathrm{Yb_2O_3}\cdot 0.01\mathrm{Y_2O_3}\cdot(0.99-x)$ ZrO_2 (with $x=0.01$, 0.02, 0.03 and 0.04) were prepared by a colloidal coating technique as developed by Yuan et al. [13], using pure monoclinic ZrO_2 nanopowder (Grade TZ-0, Tosoh, Japan), analytical grade Yb_2O_3 (99.9%, Chempur) and Y_2O_3 (99.9%, AEE) as raw materials. The appropriate amounts of Yb_2O_3 and Y_2O_3 were initially dissolved in nitric acid (analytical grade) to obtain a clear nitrate solution. Subsequently, the solution was mixed with m-ZrO_2 powder in ethanol on a multidirectional mixer (type Turbula) for 24 h, followed by rotating evaporation (type Eyela) to remove the solvent. The as-prepared powder was calcined at 800 °C for 1 h to convert the nitrates to oxides. After crushing the relatively hard agglomerates formed during calcination, ball milling in ethanol for another 24 h and rotating evaporation were performed to obtain soft agglomerated stabiliser-coated ZrO_2 powder. The dried powder was shaped into cylindrical compacts by means of vacuum packing, followed by cold isostatic pressing (CIP, EPSI, Belgium) at 300 MPa.

The compacts were sintered in air at 1350–1450 °C for 1–4 h. The bulk density of the sintered ceramics was determined by the Archimedes method in ethanol on a BP210S balance (Sartorius AG, Germany). Hardness and toughness were measured by the Vickers micro-indentation method (model 3202, Zwick, Ulm, Germany) under a load of 98 N. The formula of Anstis was used to calculate the fracture toughness,[15] using an elastic modulus (E) of 210 GPa. Polished and thermally etched surfaces were investigated by means of scanning electron microscopy (SEM, XL-30-FEG, FEI, Eindhoven, The Netherlands) to reveal the microstructure. Phase identification was carried out on polished and fractured surfaces by X-ray diffraction (XRD, 3003-TT, Seifert, Ahrensburg, Germany) using Cu Kα (40 kV, 30 mA) radiation. The amount of monoclinic and tetragonal phase was determined according to Toraya's method.[16]

3. Results and discussion

3.1. Sintering behaviour

Since the density of Yb_2O_3 (9.22 g/cm^3) is much higher than that of Y_2O_3 (5.03 g/cm^3), the bulk density of the sintered co-doped ceramics is higher than that of Y_2O_3-stabilized ZrO_2 ceramics with the same amount of dopant (~6.05 g/cm^3). The density linearly increases with increasing Yb_2O_3 content, as shown in Fig. 1. Moreover, at a fixed soaking time of 1 h, the density increased with increasing sintering temperature reaching full density at 1450 °C (see Fig. 1a), as revealed by the absence of porosity on polished cross-sectioned samples observed by SEM. Increasing the dwell time at 1450 °C up to 4 h does not influence the final density.

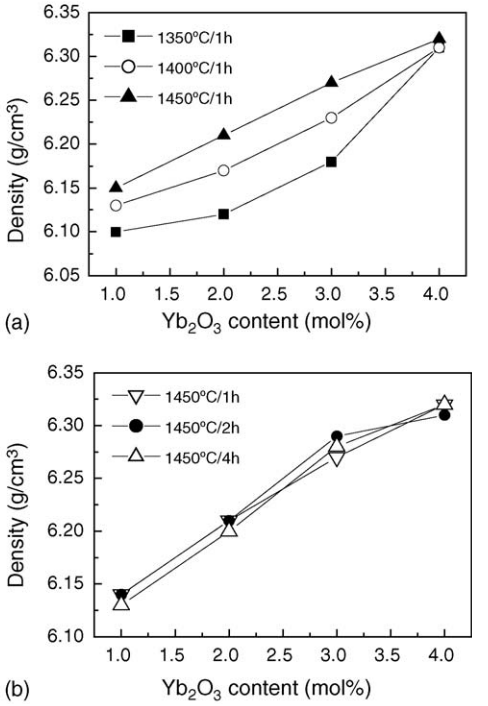

Fig. 1. Sintered density of 1.0 mol% Y_2O_3-stabilised ZrO_2 as function of the Yb_2O_3 co-stabiliser content and the sintering temperature (a) and time (b).

3.2. Phase assemblages and microstructure

The XRD patterns of the polished ceramics with 1.0 mol% Y_2O_3 and different Yb_2O_3 content sintered at 1400 °C/1 h, 1450 °C/1 h and 1450 °C/4 h are presented in Fig. 2(a)–(c), respectively. Only t or $t+c$ diffraction profiles were observed in all ceramics, except for the small amount of monoclinic (m) ZrO_2 phase in the material grade containing 1.0 mol% Yb_2O_3 sintered at 1450 °C for 4 h. According to JCPDS card 42-1164 and 27-0997, the tetragonal $(0\,0\,2)_t$ and $(1\,1\,0)_t$ diffraction peaks should appear at around $2\theta=34.5°$, whereas only the cubic $(2\,0\,0)_c$ peak is present at this 2θ value. Due to the small difference between the position of the $(1\,1\,0)_t$ and $(2\,0\,0)_c$ peaks, they often overlap, which makes it difficult to unequivocally prove the presence of cubic ZrO_2 from the XRD patterns. In the present XRD results, however, it was noticed that there were two diffraction peaks appearing at $2\theta\approx 34.5°$ for the sample with Yb_2O_3 content $\leq$3.0 mol%, independent of the sintering temperature and holding time, whereas only one peak was observed when the Yb_2O_3 content was increased to 4.0 mol%, implying the main phase in the $4.0\mathrm{Yb_2O_3}$–$1.0\mathrm{Y_2O_3}$–ZrO_2 ceramics to be cubic. To confirm this, XRD measurements were performed on the $4.0\mathrm{Yb_2O_3}$–$1.0\mathrm{Y_2O_3}$–ZrO_2 ceramics sintered for 2 h at 1450 °C in a wider 2θ range from 20 to 80°. As shown in Fig. 3, the measured XRD pattern of this sample agrees well with that of the cubic ZrO_2 (JCPDS card 27-0997) and the $(4\,0\,0)_c$ peak, which is often used to distinguish the cubic structure from the

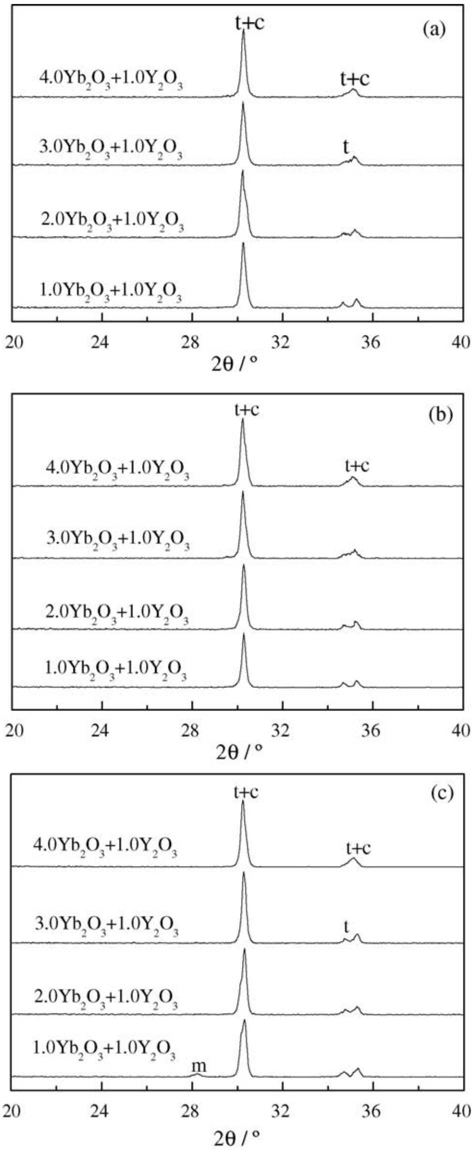

Fig. 2. XRD patterns of polished Y_2O_3 and Yb_2O_3 co-stabilised ZrO_2 ceramics sintered under different conditions: (a) 1400 °C, 1 h; (b) 1450 °C, 1 h; and (c) 1450 °C, 4 h.

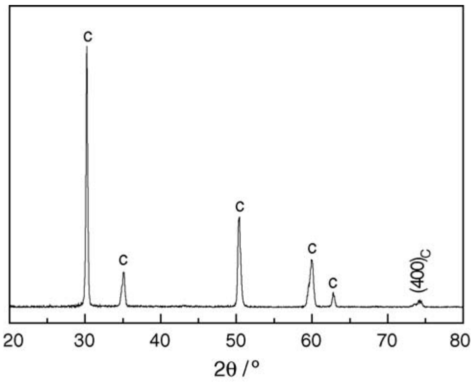

Fig. 3. XRD pattern of 4.0 mol% Yb_2O_3 and 1.0 mol%Y_2O_3 co-doped ZrO_2 ceramics sintered at 1450 °C for 2 h.

tetragonal structure, is clearly observed. To our knowledge, it has never been reported that fully dense cubic ZrO_2 (FSZ) can be obtained with only 5.0 mol% stabilizer after only 2 h of pressureless sintering in air at 1450 °C. In the binary Y_2O_3–ZrO_2 system, 8.0 mol% co-precipitated dopant and a long heat-treatment at higher temperature[17] are needed to form dense cubic ZrO_2, whereas 20 mol% co-precipitated CeO_2 is needed to obtain FSZ material in the CeO_2–ZrO_2 system.[4,18]

SEM micrographs of the thermally etched (20 min at 1300 °C) ceramics with different Yb_2O_3 content and sintered at various conditions are shown in Figs. 4–6. The material grades with 1.0 and 2.0 mol% Yb_2O_3, sintered for 1 h at 1400 °C, exhibit a similar homogenous microstructure with an average *t*-ZrO_2 grain size of about 0.3 μm. In the ceramics with 3.0 and 4.0 mol% Yb_2O_3, however, a clear bimodal grain size distribution is present, composed of a *t*-ZrO_2 matrix with fine grain size (<0.3 μm) and dispersed larger grains. The grain size significantly increases and the bimodal microstructure is more obvious with increasing sintering temperature (Fig. 5). Since no monoclinic ZrO_2 is detected by XRD analysis, it can be suggested that the larger grains are cubic ZrO_2. Increasing the holding time at 1450 °C leads to further grain growth in all ceramic grades, as shown in Fig. 6. The amount of smaller *t*-ZrO_2 grains in the ceramics with 3.0 and 4.0 mol% Yb_2O_3 is found to decrease with increasing dwell time from 1 to 2 h at 1450 °C. More specifically, less than 5 vol.% smaller grains are retained in the material grade with 3.0 mol% Yb_2O_3 and almost all disappeared in the ceramic with 4.0 mol% Yb_2O_3. The presence of only large grains in combination with the diffraction pattern presented in Fig. 3 provides strong support for the interpretation that the large grains are cubic in nature.

3.3. Mechanical properties

The Vickers hardness and indentation fracture toughness of the different ceramic grades, sintered at different conditions as a function of the Yb_2O_3 content, are summarised in Fig. 7(a) and (b), respectively. The hardness increases with increasing Yb_2O_3 content, independent of the sintering conditions. A longer sintering time at 1450 °C leads to a decreased hardness, which has to be attributed to grain growth and an increased *c*-ZrO_2 content. The hardness of the 1.0 mol% Yb_2O_3 material grade sintered for 4 h at 1450 °C is lower due to spontaneous transformation of a fraction of the *t*-ZrO_2 grains, resulting in *m*-ZrO_2 (see Fig. 2c) and concomitant microcracks.

The fracture toughness decreases with increasing Yb_2O_3 content, with a strong decrease in toughness upon increasing the Yb_2O_3 from 1.0 to 2.0 mol%. Additionally, the toughness of the ceramics co-stabilised with 1.0 mol% Yb_2O_3 increases with increasing sintering temperature and holding time, whereas it is hardly influenced for the ceramics co-stabilised with more than 2.0 mol% Yb_2O_3. It is common knowledge that the stress-induced transformation toughening mechanism plays an important role in the toughness of TZP ceramics. Both grain size and stabilizer content are factors that determine the susceptibility of the tetragonal ZrO_2 phase to stress-induced transformation and the concomitant fracture toughness of the materials.[17] The

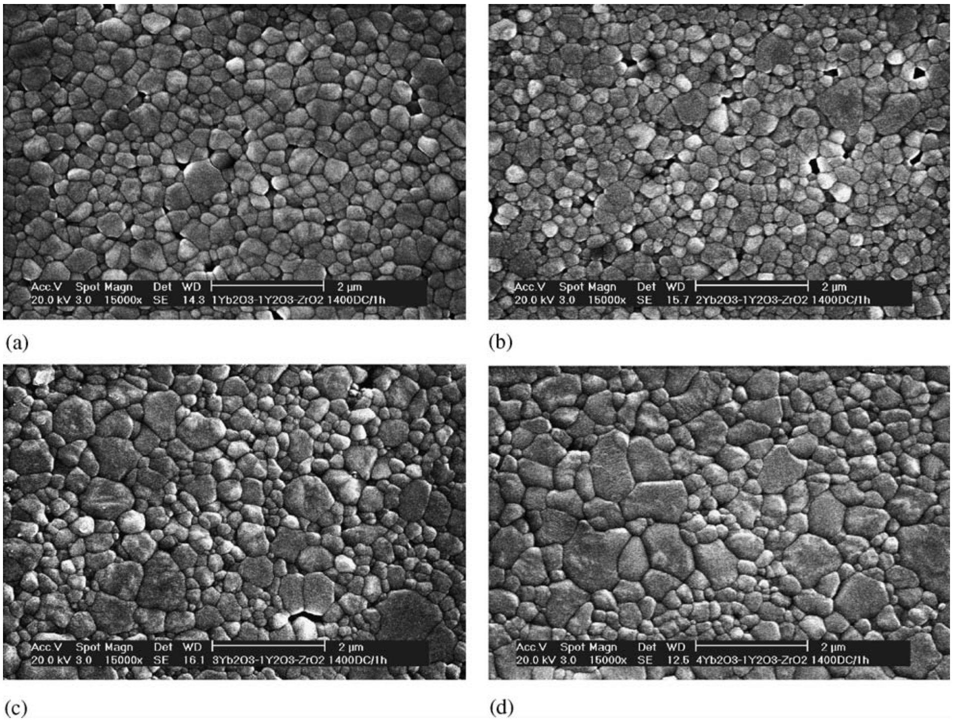

Fig. 4. SEM micrographs of 1 mol% Y_2O_3 stabilized ZrO_2 ceramics co-doped with 1.0 (a), 2.0 (b), 3.0 (c) and 4.0 (d) mol% Yb_2O_3, sintered for 1 h at 1400 °C.

increased toughness with increasing sintering temperature and holding time observed in the 1.0 mol% Yb_2O_3 containing materials can be attributed to the enhanced transformability caused by grain growth. A maximum fracture toughness of 9.5 MPa m$^{1/2}$ is reached in the 1.0 mol% Y_2O_3 and 1.0 mol% Yb_2O_3 co-stabilised ceramic sintered for 4 h at 1450 °C, since some *t*-ZrO_2 grains reached the critical grain size for spontaneous transformation as revealed by the presence of a small amount of monoclinic phase as shown in Fig. 3(c). Although the ceramic with 2.0 mol% Yb_2O_3 has a similar microstructure to that of the material grade with 1.0 mol% Yb_2O_3, the toughness is significantly lower. The results of XRD phase analysis on polished and fractured ceram-

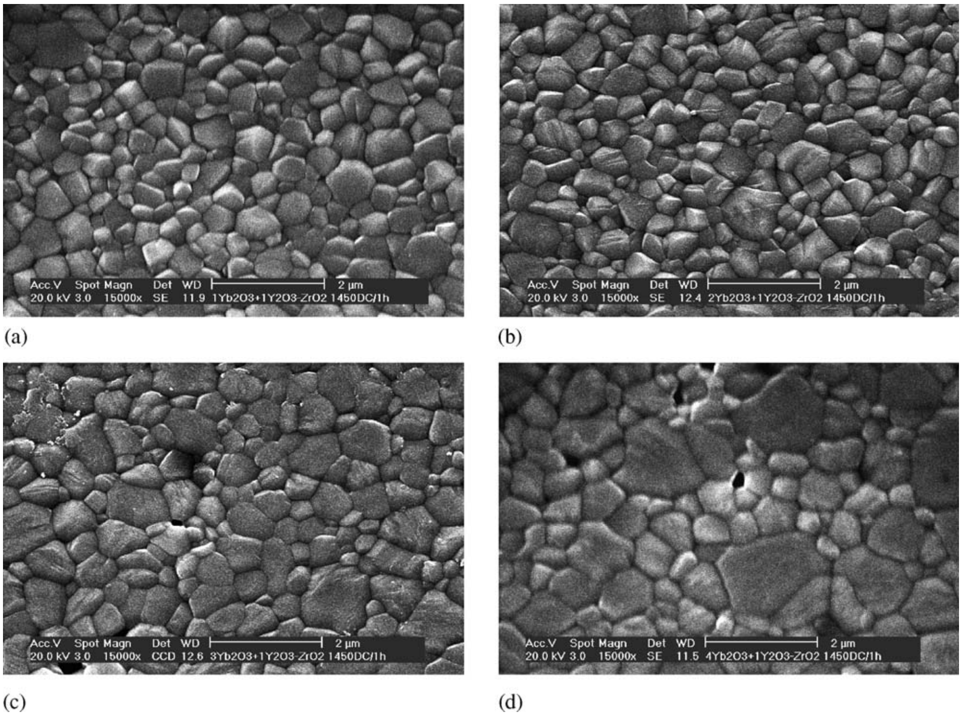

Fig. 5. SEM micrographs of 1 mol% Y_2O_3 stabilized ZrO_2 ceramics co-doped with 1.0 (a), 2.0 (b), 3.0 (c) and 4.0 (d) mol% Yb_2O_3, sintered for 1 h at 1450 °C.

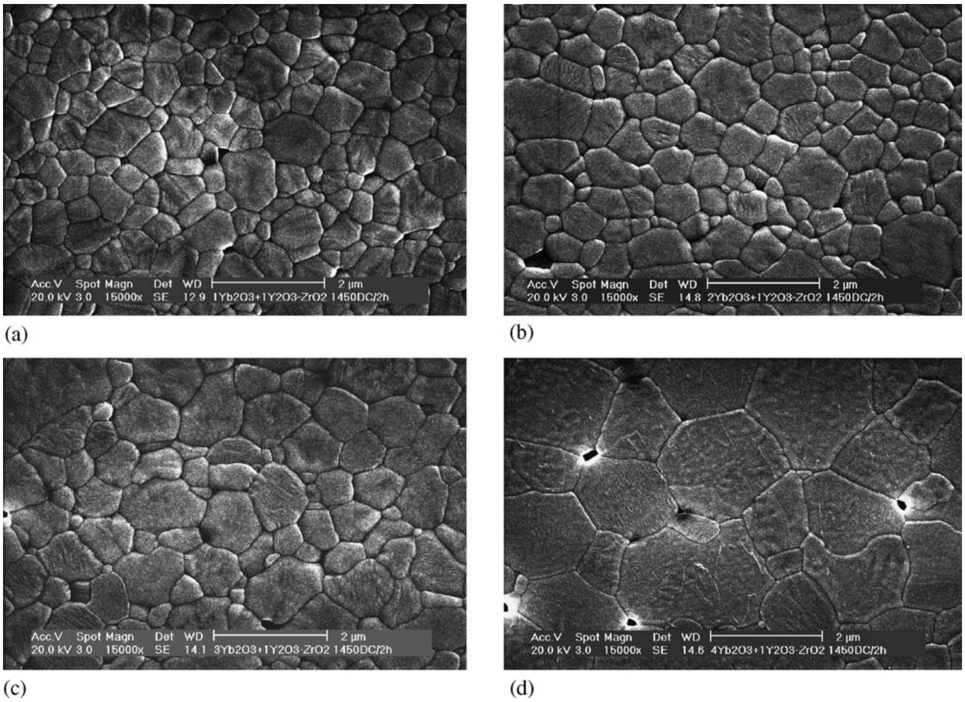

Fig. 6. SEM micrographs of 1 mol% Y_2O_3 stabilized ZrO_2 ceramics co-doped with 1.0 (a), 2.0 (b), 3.0 (c) and 4.0 (d) mol% Yb_2O_3, sintered for 2 h at 1450 °C.

ics with 1.0 and 2.0 mol% Y_2O_3 sintered for 1 h at 1450 °C, as summarised in Table 1, revealed that 50 vol.% of the *t*-ZrO_2 in the ceramic with 1.0 mol% Yb_2O_3 transformed upon fracturing, whereas only 7.23 vol.% monoclinic phase was detected upon fracturing of the 2.0 mol% Yb_2O_3 containing ceramic. These data prove that the susceptibility of the tetragonal ZrO_2 phase to stress-induced transformation in the 2.0 mol% Yb_2O_3 stabilised ceramic is much lower than that of the 1.0 mol% Yb_2O_3-stabilised ceramic, co-stabilised with 1.0 mol% Y_2O_3. The fracture toughness of the higher Y_2O_3 content ceramics with *t*- and *c*-ZrO_2 phase and concomitant bimodal grain size distribution is even lower than that of the 2.0 mol% Yb_2O_3 co-stabilised grades, independent on the investigated sintering temperature and sintering time.

Table 1
Volume percent of monoclinic and tetragonal ZrO_2 phase on polished and fractured surfaces of 1.0 mol% Y_2O_3 stabilised ceramics, co-stabilised with 1.0 and 2.0 mol% Yb_2O_3 sintered at 1450 °C for 1 h

Ceramic	Polished surface		Fracture surface	
	V_m (vol.%)	V_t (vol.%)	V_m (vol.%)	V_t (vol.%)
$1.0Yb_2O_3 + 1.0Y_2O_3$	0	100	51.14	48.86
$2.0Yb_2O_3 + 1.0Y_2O_3$	0	100	7.23	92.77

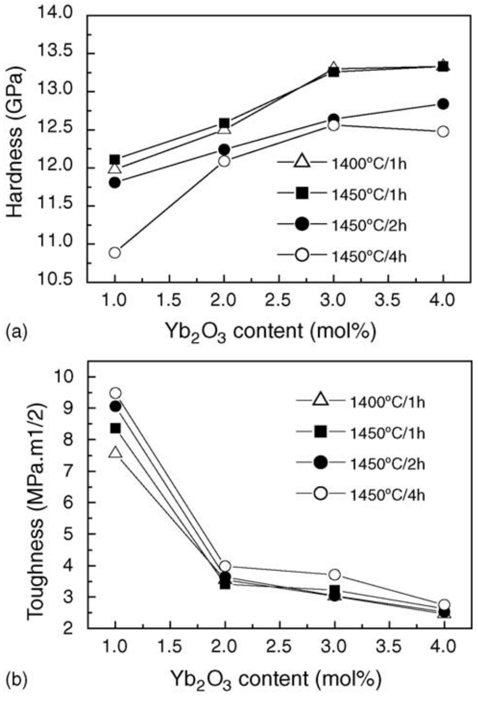

Fig. 7. Vickers hardness (HV_{10}) (a) and indentation fracture toughness (b) of 1.0 mol% Y_2O_3-stabilised and ZrO_2 ceramics as function of the Yb_2O_3 co-stabiliser content.

4. Conclusions

1.0–4.0 mol% Yb_2O_3 and 1.0 mol%Y_2O_3 co-stabilized ZrO_2 ceramics were prepared from stabilizer-coated monoclinic ZrO_2 nanopowder. Fully dense ZrO_2 ceramics could be obtained by pressureless sintering in air at 1450 °C. Fully polycrystalline tetragonal (TZP) ceramics were obtained for the 1.0 mol% Y_2O_3 materials co-stabilised with 1.0 and 2.0 mol% Yb_2O_3, whereas fully stabilised cubic (FSZ) ZrO_2 ceramics were obtained when using 4.0 mol% Yb_2O_3 co-stabiliser. The Vickers hardness of the (Yb, Y)-ZrO_2 ceramics increased with increasing Yb_2O_3 content and decreased with a longer dwell time at 1450 °C, whereas the fracture toughness decreases with increasing Yb_2O_3 content. An excellent fracture toughness of 8.5 MPa $m^{1/2}$, in combination with a hardness of 12 GPa, was obtained for the 1.0 mol% Y_2O_3 and 1.0 mol% Yb_2O_3 co-stabilised materials sintered at 1450 °C for 1 h.

Acknowledgements

This work is financially supported by the Research Fund K.U. Leuven in the framework of the Flanders-China bilateral projects BIL 02/06, BIL 04/13 and BIL 04/14.

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