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Phase stability and mechanical properties of TZP with a low mixed Nd_2O_3/Y_2O_3 stabiliser content

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Abstract

The phase assembly of 1.0–5.0 mol% Nd_2O_3-doped ZrO_2 sintered at 1400 °C revealed that the tetragonal ZrO_2 phase could not be completely stabilised. Co-stabilising of 0.5–2.5 mol% Nd_2O_3 with 0.5–1.0 mol% Y_2O_3, however, allowed the preparation of fully dense (Nd,Y)-TZP ceramics by pressureless sintering in air at 1450 °C. The mixed stabiliser monoclinic zirconia nanopowder starting material was synthesized from a suspension of neodymium nitrate, yttrium nitrate and monoclinic zirconia powder in an alcohol/water mixture. A HV_{30} hardness of 10 GPa combined with an excellent indentation toughness of 13 MPa m$^{1/2}$ could be achieved for the (1.0Nd,1.0Y)- and (1.5Nd,1.0Y)-TZP ceramics. The influence of the mixed stabiliser content on the phase stability and mechanical properties are investigated and discussed.

Keywords: ZrO_2; (Nd,Y)-TZP; Sintering; Microstructure; Mechanical properties

1. Introduction

It is well known that partially stabilised zirconia (PSZ), and in particular tetragonal zirconia polycrystalline (TZP) ceramics are of technological importance as advanced structural ceramics because of their excellent mechanical properties such as fracture toughness and bending strength, which are associated with the stress-induced tetragonal (t) to monoclinic (m) ZrO_2 phase transformation. Stabilisers such as MgO, CaO, Y_2O_3 and CeO_2 can be used to retain as much tetragonal phase as possible at room temperature. As first reported by Garvie et al.[1] and investigated by Gupta et al.,[2] Y_2O_3 has become a very important stabiliser to ZrO_2 and is the most commonly used stabiliser.

During the past 20 years, phase stability and mechanical properties of Y_2O_3-stabilised ZrO_2 have been extensively investigated. Transformation-toughened ceramics for structural applications fabricated in the binary Y_2O_3–ZrO_2 system generally contain 2–4 mol% Y_2O_3. A Y_2O_3 content below 2 mol% has never been reported to be enough to stabilise the tetragonal phase at room temperature, as a consequence of the spontaneous t- to m-ZrO_2 transformation during cooling.[3,4]

In recent years, it has been reported that new materials with optimised properties can be obtained by the addition of more than one stabiliser to ZrO_2. As an example, Boutz et al.[5] reported that the addition of CeO_2 to a Y-TZP could prevent low-temperature degradation (LTD), while retaining a relatively high fracture toughness of 7–9 MPa m$^{1/2}$. Although the influence of a secondary stabiliser to Y-TZP is complex and has not been completely understood, it is possible to fabricate new materials with excellent combination of mechanical properties by proper selection of a secondary stabiliser.

Information on the ternary Nd_2O_3–Y_2O_3–ZrO_2 system, however, is limited to the work of Hinatsu and Muromura[6] The reported isothermal section at 1600 °C, based on 65 co-precipitated samples heated in air for 15 h, is presented in Fig. 1. A tetragonal ZrO_2 region is indicated in the ZrO_2-rich corner of this section, which is of interest in the present work. In general, however, the sintering temperature used to

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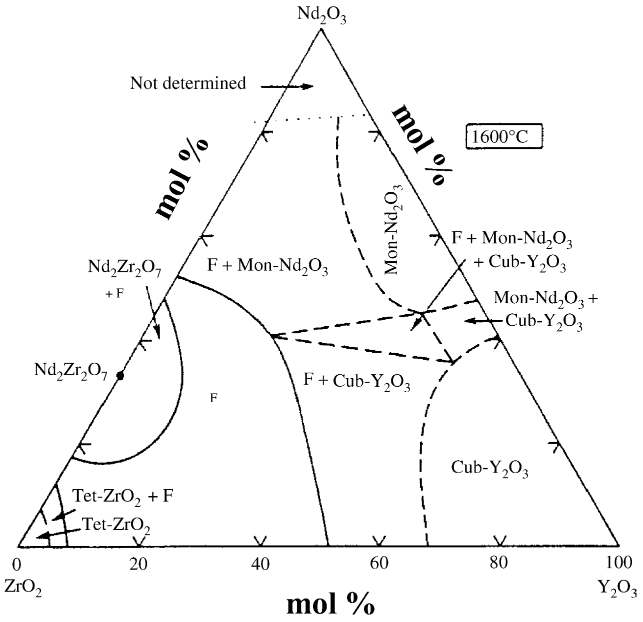

Fig. 1. Isothermal section of the Nd_2O_3–Y_2O_3–ZrO_2 system at 1600 °C.[6]

fabricate ZrO_2 ceramics with good mechanical properties is not higher than 1500 °C, limiting the usefulness of the information from this diagram. Due to the lack of experimental information on the Y_2O_3–Nd_2O_3–ZrO_2 system, it is necessary to survey the phase relationship of the ZrO_2-rich region of the binary Nd_2O_3–ZrO_2 system. Yoshimura et al.,[7] Andrievskaya and Lopato[8] and Khor and Yang[9] reported the phase equilibrium in the Nd_2O_3–ZrO_2 binary system. Due to the contradictive character of the reported information, low content Nd_2O_3-stabilised ZrO_2 nanopowders were synthesized and the phase assembly of pressureless sintered samples at 1400 °C were studied in the present work.

As reported by Khor and Yang,[9] using dc plasma spraying technique, Nd_2O_3 can stabilise the tetragonal and/or cubic ZrO_2 phase dependent on the temperature and quantity added. Due to the similarity between the ionic radius of Ce^{4+} and that of Nd^{3+} and the better resistance to reduction compared to CeO_2, it seems therefore, interesting to investigate the possibility to fabricate Nd_2O_3–Y_2O_3 co-doped ZrO_2 ceramics. A HV_{30} hardness of 10 GPa combined with a fracture toughness of 11.5 MPa $m^{1/2}$ was recently reported for a (2.0Nd,1.5Y)-TZP sintered in air for 1 h at 1450 °C.[10] This paper, however, is focussed on even lower stabiliser contents.

The properties of the starting powder play an important role on the final properties of the sintered zirconia materials. Most of the commercial Y_2O_3-doped ZrO_2 powders are synthesized by co-precipitation. In recent years, however, other techniques were reported in which Y_2O_3 is introduced by means of a coating on the ZrO_2 particles.[11,12] The bending strength and fracture toughness of Y-TZP ceramics based on Y_2O_3-coated ZrO_2 starting powders are reported to be more attractive than those of ceramics based on co-precipitated powder, when sintered under the same conditions.[11] In the present work, a colloidal processing technique was used to prepare low-Nd_2O_3/low-Y_2O_3 co-coated m-ZrO_2 starting powders. Densification was performed by pressureless sintering in air at 1450 °C. In this paper, the phase assembly of Nd_2O_3-stabilised ZrO_2 was investigated at 1400 °C and the phase stability and mechanical properties of 0.5–1 mol% Y_2O_3 co-stabilised ZrO_2 as a function of a Nd_2O_3 content between 0.5 and 2.5 mol% is reported.

2. Experimental procedure

A colloidal suspension coating technique was applied to synthesize Nd_2O_3- and $Nd_2O_3 + Y_2O_3$-coated ZrO_2 nanopowders. Chemically pure $Y(NO_3)_3{\cdot}6H_2O$ (99.9%, Aldrich) and $Nd(NO_3)_3{\cdot}6H_2O$ (99.9%, Aldrich) were used to prepare water-based stock suspensions with an yttrium and neodymium concentration of 0.1 M. The appropriate amounts were mixed with pure m-ZrO_2 (Grade TZ-0, Tosoh, Japan) nanopowder (crystal size ≈27 nm) in ethanol for 24 h. Y-TZP milling balls (Tosoh grade TZ-3Y, Japan) were added to the suspension to break the agglomerates during mixing. In order to avoid contamination, mixing was performed in polyethylene containers. After drying of the suspensions in a rotating evaporator, the powder was calcined in air at 800 °C for 1 h. Then, a second mixing in ethanol and rotating evaporation were performed to obtain soft agglomerated stabiliser-coated nanopowder. A similar coating technique was successfully applied to produce starting powders for Ce-TZP and Y-TZP ceramics.[13–15]

As-synthesized powders were shaped into cylindrical compacts by cold isostatic pressing (CIP) at 300 MPa and subsequently densified in a tube furnace (TGA-171, Cahn, USA) under an air-flow of 100 ml/min, at 1450 °C for 1 or 2 h for Nd_2O_3/Y_2O_3 co-coated ZrO_2, and at 1400 °C for 1 or 24 h for Nd_2O_3-coated ZrO_2. Thermal cycling was performed with a heating rate of 20 °C/min from 20 to 1000 °C, 10 °C/min from 1000 °C to the sintering temperature and a cooling rate of 15 °C/min.

The Archimedes' principle was used to determine the density of the sintered samples in ethanol (BP210S balance, Sartorius AG, Germany). Phase identification was carried out by X-ray diffraction (XRD, 3003-TT, Seifert, Ahrensburg, Germany) on polished surfaces using Cu Kα (40 kV, 30 mA) radiation. The m- and t-ZrO_2 volume fraction was evaluated from the diffraction patterns according to the method of Toyara et al.[16] The microstructure of thermally etched cross-sectioned samples was investigated by scanning electron microscopy (SEM, XL-30FEG, FEI, Eindhoven, The Netherlands). For SEM observation, the surface of the samples was polished and thermally etched at 1300 °C for 30 min. The average grain size was calculated from the linear intercept length of more than 1000 grains, measured by image analysis of SEM micrographs. The reported values are the actually measured mean intercept lengths. The Vickers hardness (HV_{30}) was measured on a Zwick hardness tester (model 3202, Zwick, Ulm, Germany) with an indentation load of 30 kg on polished cross-sectioned samples. The fracture toughness, K_{IC}, was obtained from the radial crack pattern generated by these HV_{30} indentations, and calculated according to the formula of Anstis et al.[17] using an elastic modulus of 200 GPa, a general value for 3Y-TZP ceramics.

3. Results and discussion

3.1. Nd_2O_3-stabilised ZrO_2

In order to investigate the tetragonal ZrO_2 phase stabilisation, 1–5 mol% Nd_2O_3 coated monoclinic ZrO_2 powder compacts were sintered at 1400 °C in air for 24 h. All sintered samples completely cracked, implying spontaneous t- to m-ZrO_2 phase transformation during cooling to room temperature. The t-ZrO_2 phase content, as obtained from XRD analysis, is plotted as function of the Nd_2O_3 content in Fig. 2. The t-ZrO_2 content increases linearly with increasing Nd_2O_3 content indicating that t-ZrO_2 might be fully stabilised by using a proper higher amount of Nd_2O_3. However, no complete retention of the tetragonal phase was achieved in the investigated Nd_2O_3 stabiliser range.

Considering the relatively long holding time of 24 h, the large amount of monoclinic phase in the sintered Nd_2O_3-doped ZrO_2 samples might be attributed to grain growth of the tetragonal phase beyond the critical size for spontaneous transformation. To study this, powder compacts of 3, 4 and 5 mol% Nd_2O_3-coated ZrO_2 were sintered at 1400 °C in air for 1 h. The phase assembly of the 1 h sintered samples is also plotted in Fig. 1. The similar monoclinic phase content in the 1 h and 24 h sintered samples indicates that the addition of up to 5 mol% Nd_2O_3 does not completely stabilise the t-ZrO_2 phase when sintering for 1 h at 1400 °C.

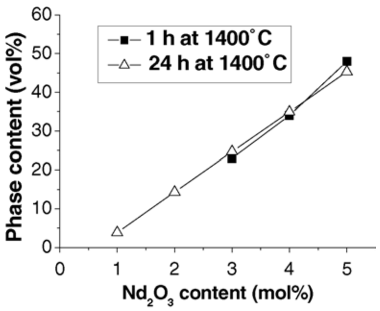

Fig. 2. Tetragonal ZrO_2 phase content of the Nd_2O_3-stabilised ZrO_2 ceramics as a function of the Nd_2O_3 content, sintered for 1 and 24 h at 1400 °C.

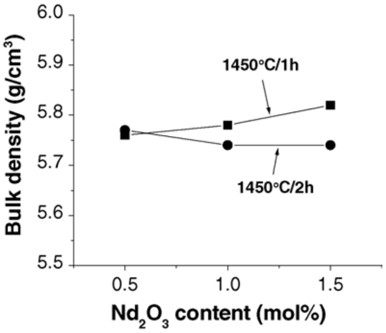

Fig. 3. Density of the (*x*Nd,0.5Y)-ZrO_2 ceramics sintered for 1 h at 1450 °C as a function of the Nd_2O_3 content.

3.2. *x* mol% Nd_2O_3–0.5 mol% Y_2O_3-stabilised ZrO_2 with *x* = 0.5, 1.0 and 1.5

All investigated (*x*Nd,0.5Y)-ZrO_2 (*x* = 0.5, 1.0 and 1.5) ceramics showed severe micro- and macrocracks after sintering from the spontaneous t- to m-ZrO_2 transformation during cooling. Fig. 3 shows the bulk density of the samples sintered at 1450 °C as a function of the Nd_2O_3 content. The measured density of the samples sintered at 1450 °C for 1 h is significantly lower than the full density, estimated to be around 6.06 g/cm^3 based on the obtained results for the 1.0 mol% Y_2O_3 co-stabilised grades, because of microcracking. At a longer sintering time of 2 h, microcracking is even more severe due to grain growth of the t-ZrO_2 phase.

These experimental results clearly indicate that 0.5 mol% Y_2O_3 in combination with 0.5–1.5 mol% Nd_2O_3 is not

Table 1
Mechanical properties, phase content and average grain size of the (*x*Nd,1.0Y)-ZrO_2 ceramics sintered at 1450 °C in air for 1 or 2 h

Ceramic	Holding time (h)	Density (g/cm^3)	HV_{30} (GPa)	K_{IC} (MPa m$^{1/2}$)	Phase assembly[a] (vol.%)	Average grain size (nm)
(0.5Nd,1.0Y)-ZrO_2	1	5.80 (cracked)	/	/	mono/s, t/m	395
	2	5.79 (cracked)	/	/	mono/s, t/m	433
(1.0Nd,1.0Y)-ZrO	1	6.06	9.99 ± 0.04	12.52 ± 1.32	95 t	284
	2	5.99 (cracked)	/	/	55 t	303
(1.5Nd,1.0Y)-ZrO	1	6.07	9.84 ± 0.24	13.06 ± 0.44	92 t	280
	2	5.88 (cracked)	/	/	23 t	308
(2.0Nd,1.0Y)-ZrO_2	1	5.98	8.95 ± 0.36	9.72 ± 1.27	92 t	275
	2	5.98 (cracked)	8.91 ± 0.30	3.54 ± 0.78	31 t	310
(2.5Nd,1.0Y)-ZrO_2	1	5.90 (cracked)	8.82 ± 0.51	6.56 ± 1.40	40 t	285
	2	5.85 (cracked)	8.60 ± 0.12	3.30 ± 0.43	37 t	322

[a] t: tetragonal ZrO_2; mono: monoclinic ZrO_2; s: strong; m: medium.

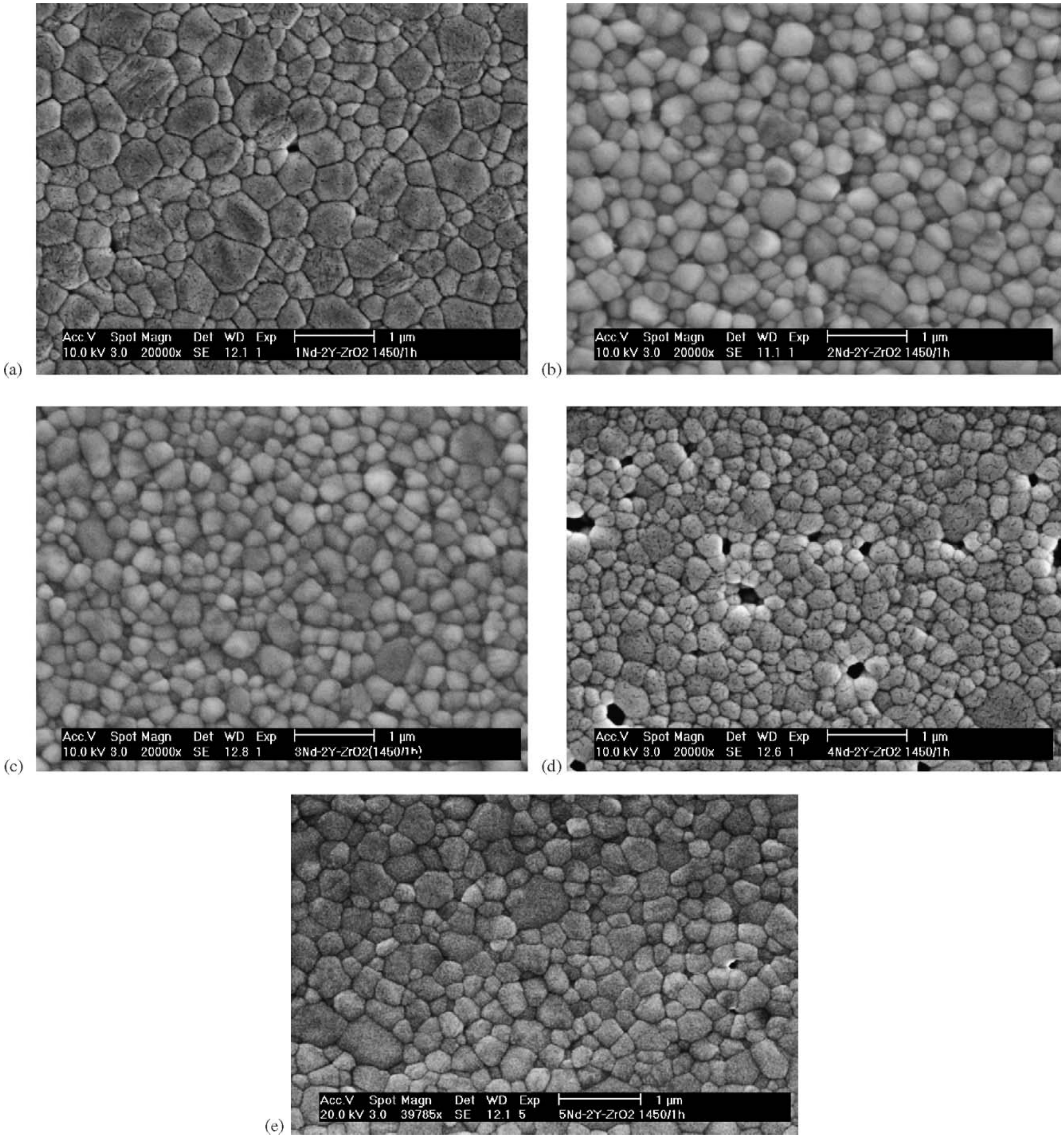

Fig. 4. Scanning electron micrographs of the (xNd,1.0Y)-ZrO_2 materials, co-stabilised with 0.5 (a), 1.0 (b), 1.5 (c), 2.0 (d) and 2.5 (e) mol% Nd_2O_3, sintered at 1450 °C for 1 h.

enough to stabilise the t-ZrO_2 phase after sintering for 1–2 h at 1450 °C. Therefore, the Y_2O_3 stabiliser content was increased to 1 mol%.

3.3. *x mol% Nd_2O_3–1.0 mol% Y_2O_3-stabilised ZrO_2 with $x = 0.5$, 1.0, 1.5, 2.0 and 2.5*

The mechanical properties, phase composition and average grain size of the investigated (xNd,1.0Y)-ZrO_2 ceramics, sintered for 1 or 2 h at 1450 °C, are summarised in Table 1. Representative SEM micrographs of the thermally etched ceramic grades are presented in Figs. 4 and 5.

For the (0.5Nd,1.0Y)-ZrO_2 composition, fully dense materials could not be obtained regardless of the sintering time. XRD analysis revealed the presence of m-ZrO_2 as the major constituent phase. The average grain size of about 0.4 μm is relatively large compared to the higher Nd_2O_3-stabilised grades, as reported in Table 1.

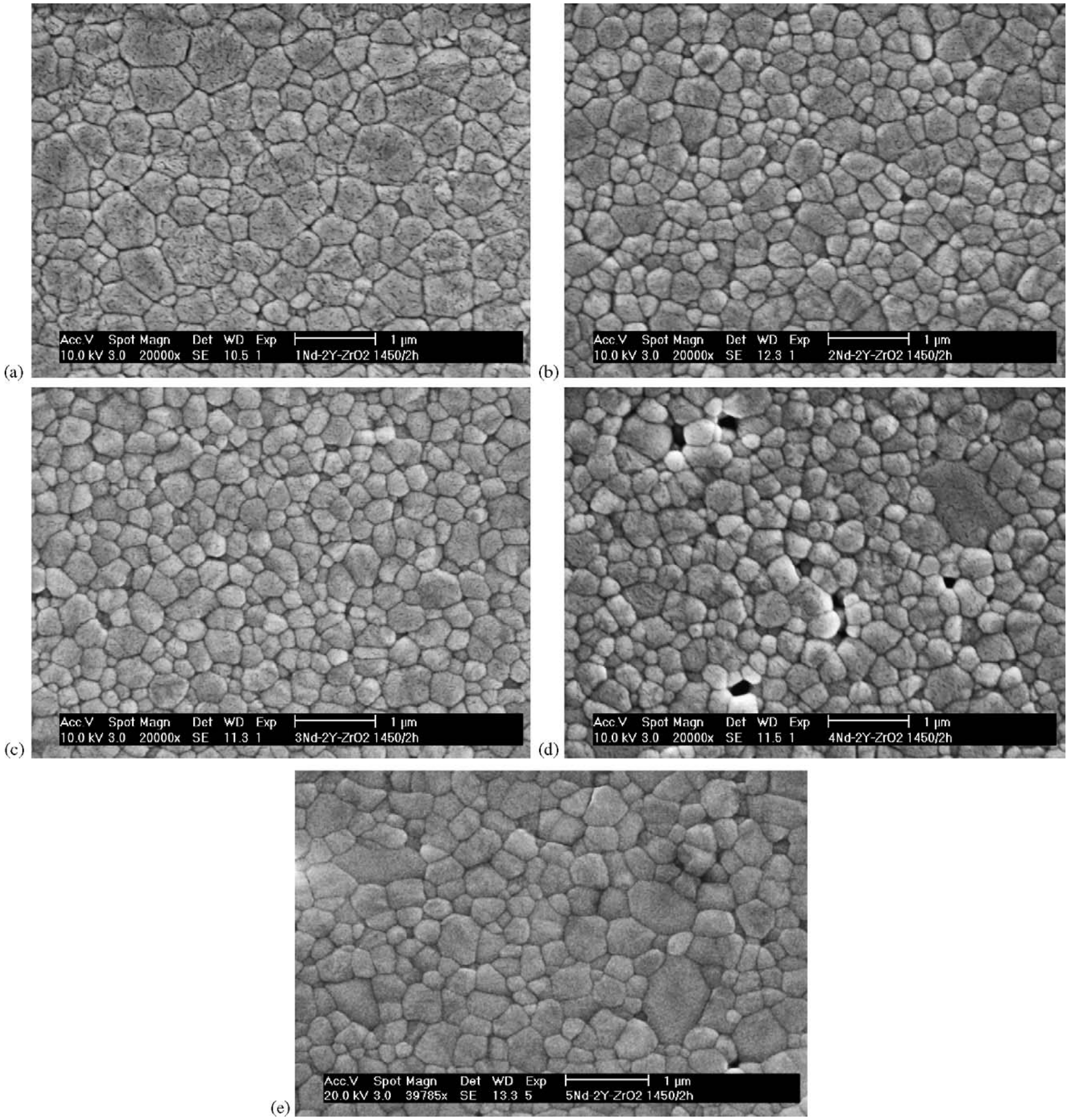

Fig. 5. Scanning electron micrographs of the (*x*Nd,1.0Y)-ZrO_2 materials, co-stabilised with 0.5 (a), 1.0 (b), 1.5 (c), 2.0 (d) and 2.5 (e) mol% Nd_2O_3, sintered at 1450 °C for 2 h.

Fully dense (1.0Nd,1.0Y)-ZrO_2 and (1.5Nd,1.0Y)-ZrO_2 ceramics, however, were obtained after sintering for 1 h at 1450 °C. The main crystalline phase is t-ZrO_2, although a small amount of m-ZrO_2 (<8 vol.%) was found that might be caused by polishing (see Table 1). The average grain size of 0.28 μm is substantially lower than for the 0.5 mol% Nd_2O_3-stabilised grade, and comparable for the 1.0 and 1.5 mol% Nd_2O_3 grades. After 2 h sintering, the density of the samples decreased and microcracks appeared. XRD analysis revealed a large amount of monoclinic ZrO_2 phase in these samples. The reduced density should, therefore, be correlated to the formation of microcracks caused by the spontaneous transformation. Although the average grain size only slightly increases to 0.30 μm, spontaneous transformation occurred indicating that the critical t-ZrO_2 grain size for spontaneous transformation of (1.0Nd,1.0Y)-ZrO_2 and (1.5Nd,1.0Y)-ZrO_2 ceramics is about 0.3 μm.

The density of the (2.0Nd,1.0Y)-ZrO_2 and (2.5Nd,1.0Y)-ZrO_2 samples, sintered for 1 h at 1450 °C are lower than that of the (1.0–1.5Nd,1.0Y)-ZrO_2 ceramics (see Table 1).

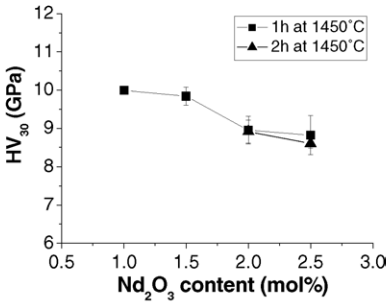

Fig. 6. Vickers hardness of the (xNd,1.0Y)-ZrO_2 samples sintered at 1450 °C as a function of the Nd_2O_3 content.

No visual cracks were observed for the (2.0Nd,1.0Y)-ZrO_2, whereas macrocracks were present in the (2.5Nd,1.0Y)-ZrO_2 ceramic.

The dependence of the Vickers hardness and indentation toughness of the 1.0 mol% Y_2O_3 co-stabilised ceramic grades as a function of the Nd_2O_3 content is graphically presented in Figs. 6 and 7, respectively. The HV_{30} hardness decreases slightly from 10 to 9 GPa with increasing Nd_2O_3 content, due to the t- to m-ZrO_2 transformation at higher Nd_2O_3 levels.

The fracture toughness of the (1.0–2.5Nd,1.0Y)-ZrO_2 ceramics is strongly related to the Nd_2O_3 content and the sintering time at 1450 °C, as shown in Fig. 7. The toughness of the 0.5 mol% Nd_2O_3 co-stabilised grade is low due to the presence of microcracks but increases with increasing Nd_2O_3 content up to a maximum of 13.04 MPa $m^{1/2}$ for a Nd_2O_3 content of 1.0 and 1.5 mol%. Beyond the maximum, the toughness decreases with increasing Nd_2O_3 content. It is well known that the excellent fracture toughness of zirconia ceramics is due to the stress-induced martensitic transformation, which is strongly related to the type and content of the stabiliser and the t-ZrO_2 grain size.[3,18] The retention of the t-ZrO_2 phase after sintering is only possible if the grain size of the dense crystalline materials is smaller than the critical size for spontaneous transformation, which depends on the stabiliser content and the amount of mechanical constraint.[19] As reported above, the (0.5Nd,1.0Y)-ZrO_2 material spontaneously transformed and the average grain size should be above the corresponding critical size. The average grain size of the (1.0–2.5Nd,1.0Y)-ZrO_2 ceramics is comparable (0.28 μm) and substantially lower than for the 0.5 mol% Nd_2O_3 co-stabilised grade, as shown in Fig. 7. The m-ZrO_2 content of the (1.0–2.5Nd,1.0Y)-ZrO_2 materials, however, increases with increasing Nd_2O_3 addition (see Table 1), indicating that the critical grain size decreases with increasing Nd_2O_3 content. The critical grain size of about 0.3 μm is exceeded in all investigated (xNd,1.0Y)-ZrO_2 ceramics after sintering for 2 h at 1450 °C, explaining the degraded samples as well as the reduced toughness of these material grades.

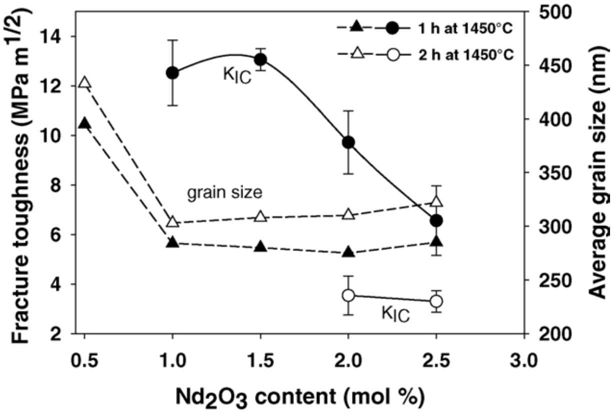

Fig. 7. Fracture toughness and average grain size of the (xNd,1.0Y)-ZrO_2 samples sintered at 1450 °C as a function of the Nd_2O_3 content.

Table 2
Volume percent of m- and t-ZrO_2 phase on polished and fractured surfaces of the (1.0Nd,1.0Y)-ZrO_2 ceramic, sintered in air at 1450 °C for 1 h

Polished surface		Fractured surface		t-ZrO_2 transformability (%)
V_m (vol.%)	V_t (vol.%)	V_m (vol.%)	V_t (vol.%)	
5	95	84	16	83

In order to investigate the transformability of the TZP material grades, the (1.0Nd,1.0Y)-ZrO_2 sample sintered for 1 h at 1450 °C was broken in a 3-point bending set-up and the phase composition was measured by X-ray diffraction. The volume percent of monoclinic and tetragonal phase measured on polished and fracture surfaces are summarised in Table 2. The tetragonal ZrO_2 phase transformability upon fracturing, i.e., the amount of tetragonal ZrO_2 that transforms during fracturing, is more than 80%, clearly illustrating the transformation toughening mechanism in this ceramic.

This work illustrated that the transformability of the t-ZrO_2 phase of a 1.0 mol% Y_2O_3 stabilised ZrO_2 can be reduced by the addition of a proper amount of Nd_2O_3 to such a level where spontaneous transformation is avoided. Moreover, by a proper selection of the mixed Y_2O_3/Nd_2O_3 stabiliser content, fully dense (Nd,Y)-TZP ceramics with excellent fracture toughness can be obtained. A maximum toughness of 13.04 MPa $m^{1/2}$ can be achieved when sintering a (1.5Nd,1.0Y)-ZrO_2 composition in air for 1 h at 1450 °C, which is well above the toughness that can be achieved for 2Y- and 3Y-TZP and comparable to the values obtained for optimised 12Ce-TZP ceramics.

4. Conclusions

Although the tetragonal ZrO_2 phase content increased linearly with increasing Nd_2O_3 content in the binary Nd_2O_3–ZrO_2 system, it was not possible to completely stabilise the t-ZrO_2 phase with up to 5 mol% Nd_2O_3 after sintering for 1 or 24 h at 1400 °C. The addition of 0.5–1.5 mol% Nd_2O_3 to a 0.5 mol% Y_2O_3 stabilised ZrO_2 or 0.5 mol% Nd_2O_3 to a 1.0 mol% Y_2O_3 stabilised ZrO_2 resulted in mainly m-ZrO_2 material after sintering for 1 h at 1450 °C.

Co-stabilising of 1.0 mol% Y_2O_3 with 1.0–2.5 mol% Nd_2O_3 allowed to obtain (Nd,Y)-TZP ceramics. A maximum indentation toughness of 13 MPa $m^{1/2}$, in combination with a HV_{30} hardness of 10 GPa, was obtained for the (1.0Nd,1.0Y)-ZrO_2 and (1.5Nd,1.0Y)-ZrO_2 ceramics sintered in air for 1 h at 1450 °C. The average ZrO_2 grain size of the ceramics sintered for 1 h was found to be comparable and around 0.28 μm at a Nd_2O_3 content of 1.0–2.5 mol%. The critical grain size for spontaneous transformation, however, decreases with increasing Nd_2O_3 content, resulting in a reduced fracture toughness and t-ZrO_2 content with increasing Nd_2O_3 addition. At lower Nd_2O_3 content, the average grain size was measured to be significantly larger resulting in spontaneous transformation.

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