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Characterization of (Nd,Y)-TZP ceramics prepared by a colloidal suspension coating technique

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Abstract

A stabiliser coating technique was applied to prepare mixed $Nd_2O_3 + Y_2O_3$ coated ZrO_2 nanopowder from an alcohol/water based suspension of neodymium nitrate, yttrium nitrate and monoclinic zirconia nanopowder. The mixed stabiliser starting powders could be fully densified into (Nd,Y)-TZP ceramics by pressureless sintering in air at 1450 °C. The obtained ceramics revealed an excellent fracture toughness up to 12.8 MPa m$^{1/2}$ in combination with a hardness of 11 GPa, a toughness that is comparable to that of the traditional 12 mol CeO_2-stabilised TZP but with higher hardness.

Keywords: Grain size; Mechanical properties; Microstructure; Sintering; ZrO_2

1. Introduction

Tetragonal zirconia polycrystalline (TZP) ceramics, especially stabilised by yttria (Y-TZP), are important and attractive engineering materials because of their excellent fracture toughness and strength. Y-TZP's however often suffer from low-temperature degradation (LTD) because of the spontaneous transformation from the tetragonal to monoclinic phase when exposed in humid atmosphere or hot aqueous solutions for a long period of time.[1,2] In recent years, new TZP materials with optimised properties obtained by the addition of more than one stabiliser have been reported. Boutz et al.[3] reported that the addition of CeO_2 to a Y-TZP could prevent LTD, while retaining a relatively high fracture toughness of 7–9 MPa m$^{1/2}$.

The most commonly used method for the synthesis of yttria-stabilised zirconia starting powder is co-precipitation. In recent years, other techniques were reported in which yttria is introduced by means of a coating on the zirconia particles.[4,5] The bending strength and fracture toughness of Y-TZP ceramics based on yttria-coated zirconia starting powder are reported[4] to be more attractive than those of ceramics based on co-precipitated powder, when sintered under the same conditions, and the excellent toughness of coated powder based Y-TZP is attributed to the inhomogeneous stabiliser distribution which results in ZrO_2 grains with a tetragonal shell around a monoclinic core.[4,5]

The possibility of forming TZP ceramics by means of co-stabilising with low amounts of neodymia and yttria was recently reported.[6–8] In the present work, 0.5–2.0 mol% Nd_2O_3 was added in combination with 1.5 mol% Y_2O_3 in order to explore the fabrication of (Nd,Y)-TZP ceramics. The stabilisers were introduced in the starting powder by means of a suspension coating technique. The prepared starting powders were pressureless sintered in air and the microstructure and mechanical properties of the fully densified ceramics were investigated.

2. Experimental procedure

A colloidal suspension coating technique was used to synthesize $Nd_2O_3 + Y_2O_3$ co-coated ZrO_2 nanopowder. Chemically pure $Nd(NO_3)_3{\cdot}6H_2O$ (99.9%, Aldrich) and $Y(NO_3)_3{\cdot}6H_2O$ (99.9%, Aldrich) were used to prepare water-based stock suspension with an yttrium and neodymium concentration of 0.1 M. The appropriate amount of suspension was mixed on a multidirectional mixer (Turbula type) with pure m-ZrO_2 nanopowder

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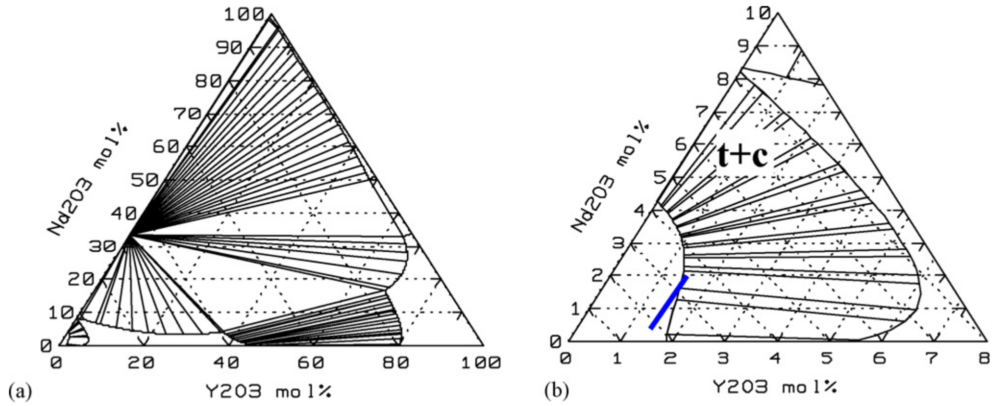

Fig. 1. Calculated ternary ZrO_2–Nd_2O_3–Y_2O_3 phase diagram at 1450 °C (a) and a detail of the ZrO_2-rich corner (b). The investigated composition region is indicated by the line in b.

with a crystal size of ~27 nm (Tosoh grade TZ-0, Japan) in ethanol in a polyethylene container for 24 h. Y-TZP milling balls (Tosoh grade TZ-3Y, Japan) were added to the suspension to break the agglomerates during mixing. After drying by rotation evaporation, the powder was calcined in air at 800 °C for 1 h. After calcination, a second mixing in ethanol and rotating evaporating were performed to obtain soft agglomerated stabiliser-coated nanopowder. The coating technique was already successfully applied to produce starting powders for Ce-TZP and Y-TZP ceramics.[9–11]

The coated 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, for 1–8 h at 1450 °C. Thermal cycling was performed with a heating rate of 20 °C/min from 20 to 1000 °C, 10 °C/min from 1000 to 1450 °C and a cooling rate of 15 °C/min.

The Archimedes' principle was applied to determine the density of the sintered bodies 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 of the sintered ceramics. The microstructure of thermally etched (20 min in air at 1350 °C) cross-sectioned samples was investigated by scanning electron microscopy (SEM, XL-30FEG, FEI, Eindhoven, The Netherlands). 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 indentation 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.[12] using an elastic modulus of 200 GPa.

3. Results and discussion

The ternary ZrO_2–Nd_2O_3–Y_2O_3 phase diagram at 1450 °C, calculated using Thermo-Calc software, is presented in Fig. 1a and the investigated composition region, ranging from 0.5 to 2 mol% Nd_2O_3 at a constant Y_2O_3 level of 1.5 mol%, is indicated on the ZrO_2-rich part of the phase diagram in Fig. 1b. The investigated compositions are mainly located in the single-phase tetragonal ZrO_2 area.

The density of the sintered ceramics is summarised in Table 1, revealing a full density in-between 6.06 and 6.10 g/cm^3. All ceramics reached full density, except the 1.5 and 2 mol% Nd_2O_3 ceramics sintered for 1 h at 1450 °C, due to a residual monoclinic ZrO_2 content, as revealed by X-ray diffraction analysis. The critical ZrO_2 grain size for spontaneous ZrO_2 phase transformation for the 0.5, 1.0, 1.5 and 2.0 mol% Nd_2O_3 + 1.5 mol% Y_2O_3 ceramics is reached after, respectively, 8, 6, 5 and 4 h of sintering at 1450 °C, as revealed by the reduced density

Table 1
Density, hardness and indentation toughness of the 0.5–2.0 mol% Nd_2O_3 + 1.5 mol% Y_2O_3 co-doped ZrO_2 as function of the Nd_2O_3 content and the sintering time at 1450 °C

Nd_2O_3 (mol%)	Sinter time (h)	Density (g/cm^3)	HV_{30} (GPa)	K_{IC} (MPa m$^{1/2}$)
0.5	1	6.09	11.00 ± 0.08	5.63 ± 0.48
1.0	1	6.10	11.05 ± 0.17	4.86 ± 0.37
1.5	1	5.88	9.84 ± 0.06	3.72 ± 0.06
2.0	1	5.90	9.46 ± 0.23	3.29 ± 0.06
0.5	2	6.07	10.73 ± 0.12	6.88 ± 0.36
1.0	2	6.09	10.81 ± 0.06	7.23 ± 0.36
1.5	2	6.09	10.81 ± 0.06	8.40 ± 0.37
2.0	2	6.09	10.49 ± 0.15	9.68 ± 0.30
0.5	3	6.08	10.50 ± 0.21	7.93 ± 0.63
1.0	3	6.10	11.02 ± 0.06	8.94 ± 0.36
1.5	3	6.08	11.05 ± 0.08	11.14 ± 0.61
2.0	3	6.09	10.31 ± 0.17	11.53 ± 0.33
0.5	4	6.08	10.76 ± 0.10	8.78 ± 0.39
1.0	4	6.10	10.39 ± 0.14	10.95 ± 0.46
1.5	4	6.08	10.33 ± 0.06	11.01 ± 0.32
2.0	4	5.96	9.77 ± 0.48	2.44 ± 0.84
0.5	5	6.06	10.48 ± 0.29	10.01 ± 0.37
1.0	5	6.07	11.01 ± 0.13	12.84 ± 0.22
1.5	5	5.87	10.05 ± 0.18	4.57 ± 0.27
2.0	5	5.85	Cracked	Cracked
0.5	6	6.05	10.36 ± 0.03	12.14 ± 0.24
1.0	6	5.88	9.45 ± 0.09	3.40 ± 0.28
0.5	7	6.05	10.40 ± 0.05	12.28 ± 0.37
1.0	7	5.87	Cracked	Cracked
0.5	8	5.99	10.30 ± 0.07	11.88 ± 0.48

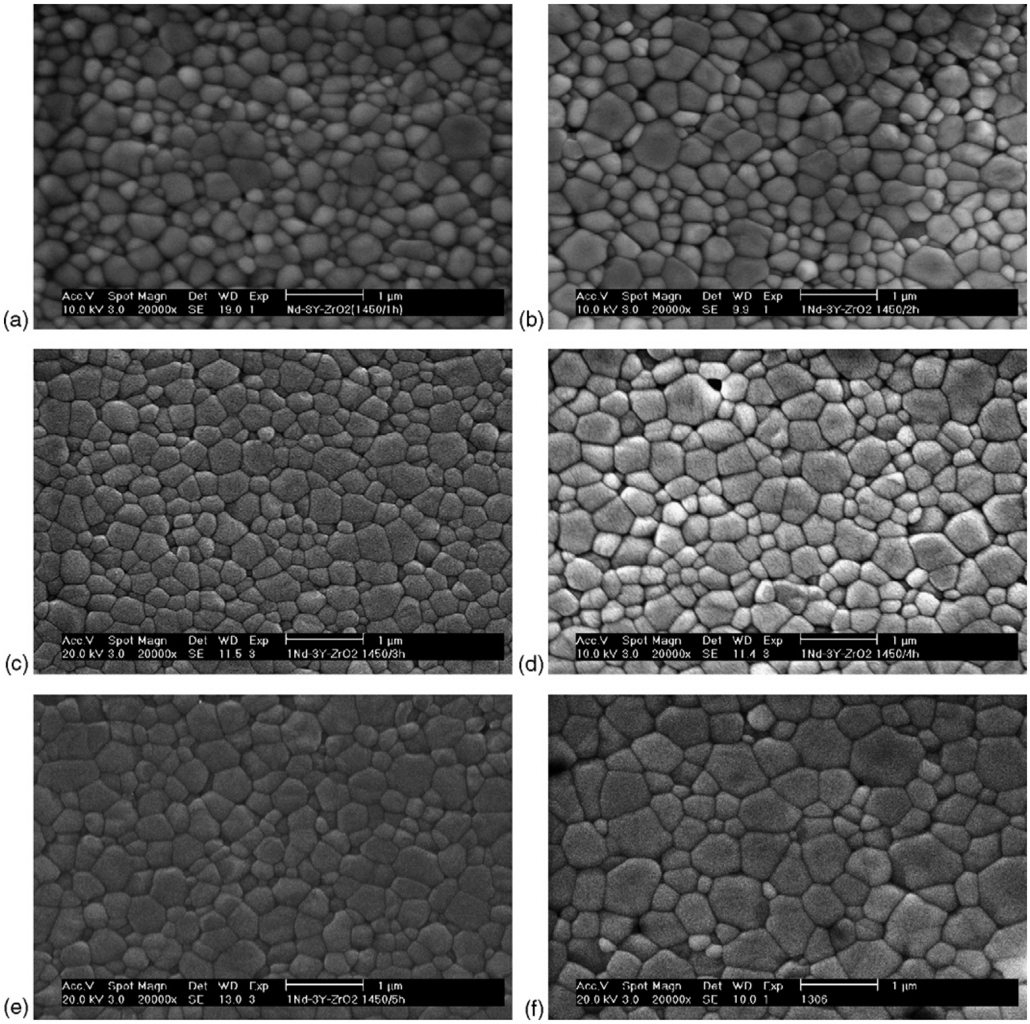

Fig. 2. SEM micrographs of the thermally etched microstructures of the 0.5 mol% Nd_2O_3 + 1.5 mol% Y_2O_3 co-doped ZrO_2 ceramics, sintered for 1 h (a), 2 h (b), 3 h (c), 4 h (d), 5 h (e) and 6 h (f) at 1450 °C.

(see Table 1) resulting from the spontaneous transformation of tetragonal to monoclinic ZrO_2, which is confirmed by XRD analysis.

It is interesting to note that the addition of 0.5 up to 2.0 mol% Nd_2O_3 to a 1.5 mol% Y_2O_3 stabilised ZrO_2 allows to stabilise the t-ZrO_2 phase at room temperature. The combined Nd_2O_3–Y_2O_3 stabiliser results in fully tetragonal ZrO_2 ceramics, which can be defined as (Nd,Y)-TZP.

Representative scanning electron micrographs of the thermally etched cross-sections of the 0.5 and 1.5 mol% Nd_2O_3 + 1.5 mol% Y_2O_3 co-stabilised materials are presented in Figs. 2 and 3, respectively.

The ZrO_2 grain size of both material grades clearly increases with increasing sintering temperature. The grain size of the 1.5 mol% Nd_2O_3 co-stabilised material (see Fig. 3) is significantly lower than that of the 0.5 mol% Nd_2O_3 doped material (see Fig. 2) at the same sintering time. The critical grain size for spontaneous transformation however is already reached after 5 h of sintering at a Nd_2O_3 content of 1.5 mol%, compared to 8 h for the 0.5 mol% Nd_2O_3 material. At higher stabiliser contents, the grain size distribution becomes bimodal and is composed of larger c-ZrO_2 grains in a much finer grained t-ZrO_2 matrix, as shown in Fig. 3c and d. The presence of a small amount of c-ZrO_2 in the 1.5 and 2.0 mol% Nd_2O_3 co-stabilised ceramics is in agreement with the calculated phase diagram (see Fig. 1b).

The indentation toughness and Vickers hardness of the investigated (Nd,Y)-ZrO_2 ceramics is graphically presented as a function of the Nd_2O_3 content and the sintering temperature at 1450 °C in Figs. 4 and 5, respectively.

An excellent fracture toughness of about 11 MPa $m^{1/2}$ was obtained for all neodymia + yttria stabilised material grades. The maximum toughness for the 0.5, 1.0, 1.5 and 2.0 mol% Nd_2O_3 + 1.5 mol% Y_2O_3 co-stabilised ZrO_2 ceramics is reached after, respectively, 6, 5, 4 and 3 h sintering at 1450 °C. At longer sintering times, the tetragonal ZrO_2 phase spontaneously starts to transform due to the fact that part of the grains exceeded the critical grain size for spontaneous transformation. The concomitant formation of microcracks is in agreement with a reduced density, as summarised in Table 1. The maximum in fracture

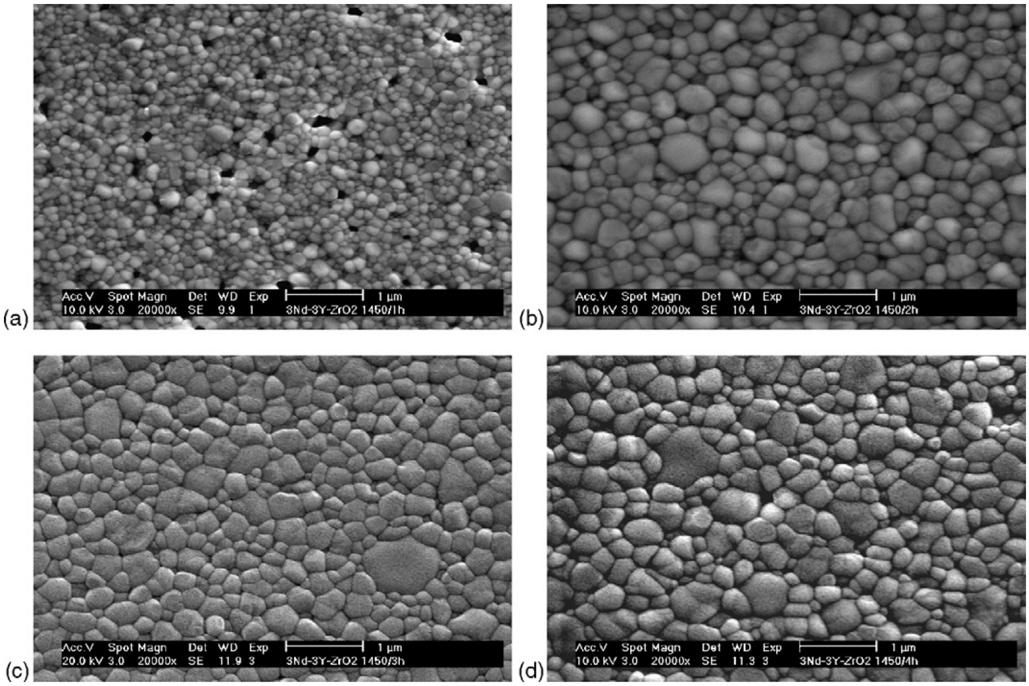

Fig. 3. SEM micrographs of the thermally etched microstructures of the 1.5 mol% Nd_2O_3 + 1.5 mol% Y_2O_3 co-doped ZrO_2 ceramics, sintered for 1 h (a), 2 h (b), 3 h (c) and 4 h (d) at 1450 °C.

toughness is in agreement with the general observations in the Y-TZP system.[13]

The Vickers hardness is relatively constant at around 10.5 GPa. The hardness decreases at longer sintering times due to spontaneous transformation, whereas it is also lower for the 1.5 and 2.0 mol% Nd_2O_3 co-stabilised materials sintered for 1 h due to the residual monoclinic ZrO_2 content.

The obtained (Nd,Y)-TZP ceramics have a slightly lower hardness than 3Y-TZP (12 GPa), but a higher hardness than 12Ce-TZP (9 GPa), whereas the indentation toughness is higher than that of Y-TZP (a maximum of 9.5 MPa m$^{1/2}$) and comparable to that of an optimised 12Ce-TZP.

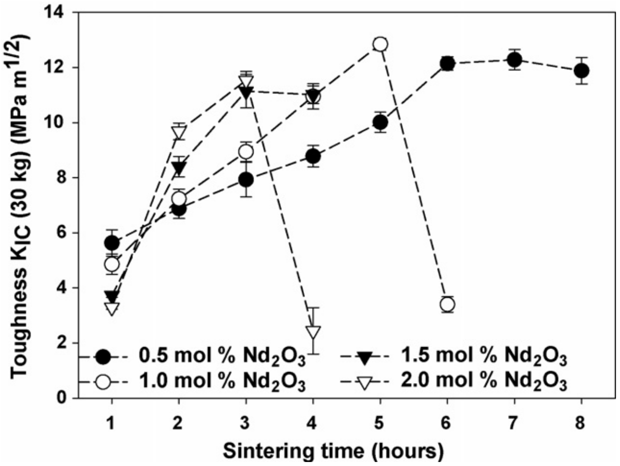

Fig. 4. Indentation toughness of the 1.5 mol% Y_2O_3 co-stabilised ceramics as a function of the Nd_2O_3 stabiliser content and the sintering time at 1450 °C.

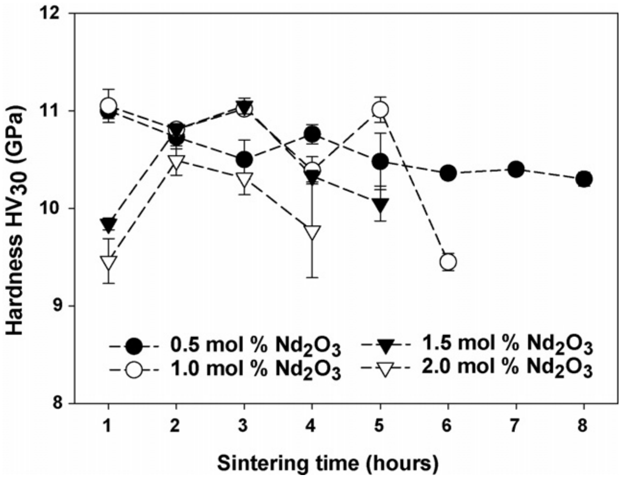

Fig. 5. Vickers hardness (HV_{30}) of the 1.5 mol% Y_2O_3 co-stabilised ceramics as a function of the Nd_2O_3 stabiliser content and the sintering time at 1450 °C.

4. Conclusions

Fully dense (Nd,Y)-TZP ceramics can be obtained by pressureless sintering in air at 1450 °C of 0.5–2.0 mol% Nd_2O_3 + 1.5 mol% Y_2O_3-coated monoclinic zirconia nanopowders, prepared from a suspension of neodymium nitrate, yttrium nitrate and pure ZrO_2 nanopowder.

An excellent fracture toughness up to 12.8 MPa m$^{1/2}$ in combination with a Vickers hardness of 11 GPa can be obtained by judicious selection of the sintering time. The optimum sintering time was found to increase with decreasing Nd_2O_3 co-stabiliser content, whereas the critical grain size for spontaneous transformation decreases with increasing Nd_2O_3 content.

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