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Hydrothermal stability of mixed stabilised tetragonal (Y, Nd)-ZrO_2 ceramics

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ABSTRACT

Yttria + neodymia co-stabilised tetragonal ZrO_2 ceramics were developed in an attempt to improve the low temperature degradation resistance of classical Y-TZP ceramics. The influence of the partial substitution of Y^{3+} by Nd^{3+} on the phase composition, crystallography, microstructure and mechanical properties was assessed by comparison with 2Y and 3Y-TZP ceramics. Moreover, the hydrothermal stability was tested during 21 h in steam at 200 °C. Although the (Y, Nd)-TZP ceramics are not hydrothermally stable, the phase transformation is limited to the surface region of the material avoiding complete degradation as observed for Y-TZP ceramics. The improved stability is explained in terms of an expanded unit cell parameter and reduced T_0 temperature.

1. Introduction

The addition of oxides, such as Y_2O_3, lower the tetragonal (t) to monoclinic (m) phase transformation temperature in zirconia (ZrO_2) ceramics, hereby stabilising the t phase at room temperature and allowing ZrO_2 to be used as a bulk structural material [1]. However, t-ZrO_2 remains metastable and is able to transform under an applied mechanical stress. The volumetric expansion that accompanies this phase transformation induces compressive stresses at a crack tip, hereby increasing the fracture toughness of the material in a process called transformation toughening [2]. The use of tetragonal Y-ZrO_2 (Y-TZP) ceramics as a biomaterial however is limited since Y-TZP often suffers from a slow t to m transformation at the sample surface in a humid atmosphere, followed by microcracking and loss of strength [3]. This process, recently reviewed in [4], is better known as low temperature degradation (LTD) or aging.

The most important factors enhancing the susceptibility of the material to LTD are humidity and increased t-ZrO_2 phase transformability, either induced by a decreased stabilizer content or an increased grain size [5]. Several mechanisms have been claimed in literature [4,6]. The earlier models explaining the LTD behaviour in terms of the reaction between water and yttria during aging are obsolete and the role of internal stresses associated with the diffusion of moisture species into the ZrO_2 lattice has been demonstrated [7]. LTD is now considered to be a relaxation process of the internally strained lattice by thermally activated oxygen vacancy diffusion [3,4].

The subject of this paper is to explore the development of metastable tetragonal ZrO_2 ceramics with improved hydrothermal stability. The aim is to partially replace the Y^{3+} stabiliser with cations of the same valence and size and investigate their influence on the crystallography and hydrothermal stability of ZrO_2 ceramics.

2. Experimental procedures

Monoclinic ZrO_2 nanopowder (grade TZ-0, Tosoh, Japan) was coated with 2 or 3 mol% (Y_2O_3) or co-stabilised with 1 mol% Y_2O_3 + 1–2 mol% Nd_2O_3 [8]. The proper amount of Y_2O_3 (99.9%, Acros, Geel, Belgium) and Nd_2O_3 (99.9%, Chempur, Karlsruhe, Germany) was dissolved in nitric acid (65%, Sigma–Aldrich, Bornem, Belgium). The nitrate-coated powder was calcined in air at 800 °C for 30 min. The calcined powder was additionally mixed on a multidirectional mixer (type T2A, Basel, Switzerland) in ethanol in a polyethylene container for 24 h at 60 rpm. 3Y-TZP milling balls (grade TZ-3Y, Ø 4–5 mm, Tosoh, Tokyo, Japan) were added to the container to break the agglomerates in the calcined ZrO_2 powder. The powders were densified by means of pulsed electric current sintering (PECS, type HP D 25/1, FCT Systeme, Rauenstein, Germany) for 3 min at 1450 °C and 62 MPa with a heating rate of 400 °C/min up to 1050 °C and 200 °C/min up to 1450 °C. Details of the experimental setup and temperature control are provided elsewhere [9].

Thermally etched (20 min at 1350 °C in air) polished samples were microstructurally investigated by scanning electron microscopy (SEM, XL-30 FEG, FEI, Eindhoven, The Netherlands). X-ray diffraction (Seifert 3003 T/T, Ahrensburg, Germany) was used for phase identification and calculation of the relative monoclinic and tetragonal ZrO_2 phase content according to the method of Toraya et al. [10]. The transformability of a ceramic is defined as the difference in m-ZrO_2 content of a fractured and polished surface, whereas the transformability during hydrothermal aging is the % m-ZrO_2 difference between the steam treated and pristine polished surface. The Vickers hardness, HV_{10} was measured (Model FV-700, Future-Tech Corp., Tokyo, Japan) with an indentation load of 98 N and a dwell time of 10 s. The indentation toughness was calculated according to the formula of Anstis et al. [11]. The reported values are the mean and standard deviation of 10 indentations. The elastic modulus was measured by the resonance frequency method [12].

Low temperature degradation (LTD) tests were performed at 200 °C in a saturated H_2O pressure of 1.55 MPa. Polished rectangular bars (20 mm × 5 mm × 2 mm) were inserted in a stainless steel autoclave heated in a molten salt bath.

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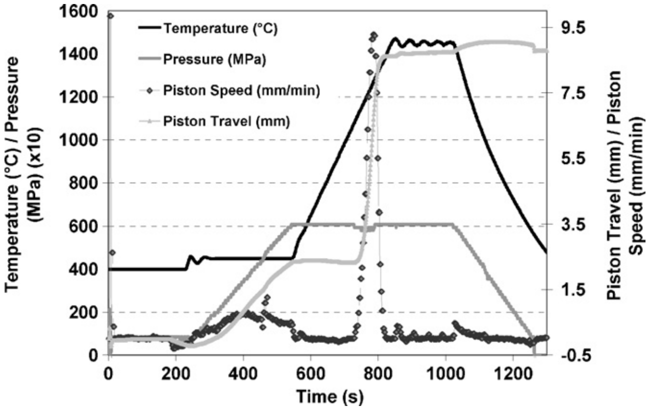

Fig. 1. Typical densification behaviour of (Y, Nd)-ZrO_2, PECS at 1450 °C for 3 min under a mechanical load of 60 MPa.

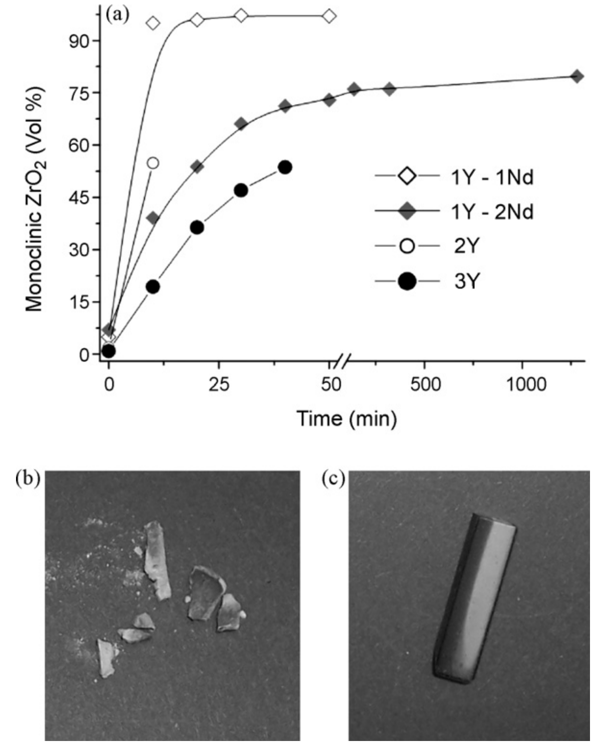

Fig. 3. Evolution of the m-ZrO_2 content on the surface of the initially polished material grades as a function of the residence time in steam at 200 °C (a) and sample morphology of a 3Y-TZP (b) and (1Y, 2Nd)-TZP (c) ceramic after 1280 min hydrothermal testing.

3. Results

3.1. Processing and characterisation

Both the Y_2O_3 and mixed Y_2O_3/Nd_2O_3-stabilised compositions were densified by PECS at 1450 °C. The maximum mechanical pressure of 60 MPa was applied during a 3-min long dwell period at 1450 °C. All investigated compositions showed a similar densification behaviour as shown in Fig. 1 for the (1Y, 2Nd)-ZrO_2 ceramic. Densification was initiated at 1080 °C. A maximum densification rate was obtained at about 1290 °C, while full density was obtained at the beginning of the dwell period at 1450 °C.

All investigated ZrO_2 grades were fully dense since no residual porosity could be observed on polished cross-sections by means of SEM, as indicated in Fig. 2. The evolution of the density in Table 1 should therefore be attributed to the stabilizer additions. The grain size of the 1 mol% Y_2O_3 grades co-stabilised with Nd_2O_3 decreases with increasing Nd_2O_3 content, as shown in Fig. 2. The grain size of the co-stabilised ceramics however is smaller than that of the 2Y and 3Y-TZP grades. The polished surface of the a of (1Y, 2Nd), (1Y, 1Nd), 2Y and 3Y grades have respectively a monoclinic ZrO_2 content of 7, 5, 2 and 1%, as shown in Fig. 3(a).

The mechanical properties of the different ceramic grades are summarised in Table 1. The Vickers hardness of the Y_2O_3-stabilised materials is higher compared to the mixed stabilised compositions, as also observed in pressureless sintered compositions [13]. The fracture toughness of all compositions scaled very well with

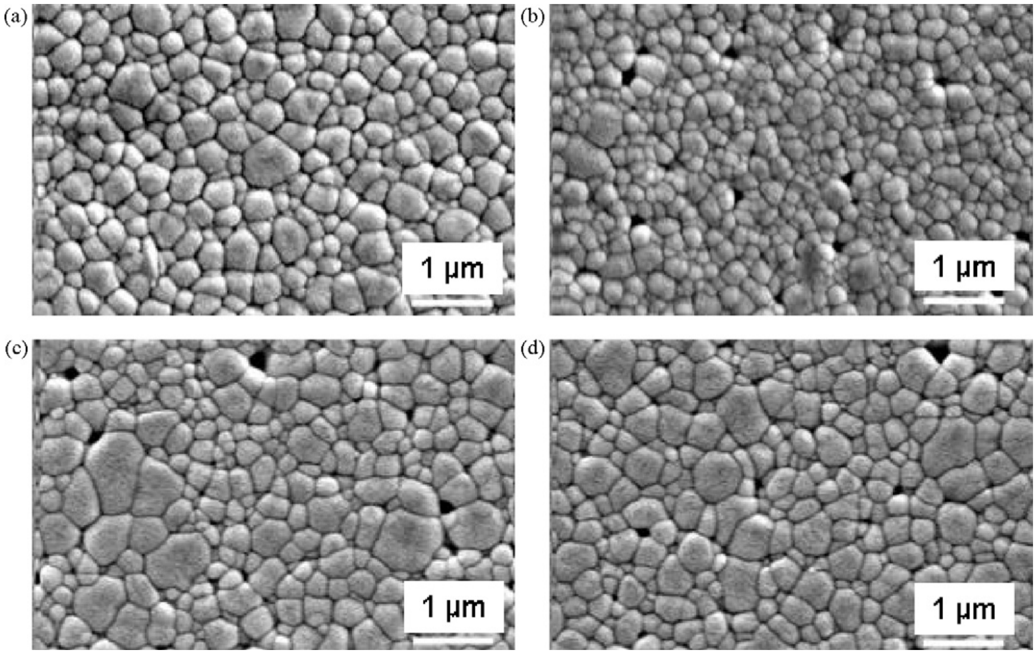

Fig. 2. Secondary electron micrographs of co-stabilised (1Y, Nd)-ZrO_2 ceramics with 1 mol% (a) and 2 mol% (b) Nd_2O_3, together with 2 mol% (c) and 3 mol% (d) Y_2O_3 coated ZrO_2 powder based ceramics.

Table 1
Mechanical properties and t-ZrO_2 phase transformability of the different (Y, Nd)-TZP and Y-TZP ceramics.

Stabilizer (mol%)	Density (g/cm^3)	E (GPa)	K_{Ic} (MPa m$^{1/2}$)	Transformability (%)	HV (kg/mm^2)
1Y-1Nd	5.97	179	7.4 ± 0.5	63.9	1076 ± 48
1Y-2Nd	6.03	180	5.9 ± 0.2	51.1	1117 ± 47
2Y	5.99	170	4.1 ± 0.1	5.2	1259 ± 4
3Y	5.98	185	4.0 ± 0.2	4.0	1297 ± 13

the t-ZrO_2 phase transformability, indicating that transformation toughening is the main toughening mechanism in this type of materials [2]. The mixed stabiliser compositions showed a substantially higher transformability and fracture toughness than the Y_2O_3-stabilised compositions. A high toughness of 7.4 ± 0.5 MPa m$^{1/2}$ was obtained for the (1Y, 1Nd)-ZrO_2 material, despite the relatively small t-ZrO_2 grain size (Fig. 2(a)). The ZrO_2 transformation behaviour was studied by thermo-mechanical analyses (TMA, Q400, T.A. Instruments) between −150 and 800 °C.

3.2. Hydrothermal stability

The hydrothermal stability of the different materials was tested in an autoclave at 200 °C. The evolution of the m-ZrO_2 phase content on an originally polished surface was measured using XRD after different exposure times in steam, as summarised in Fig. 3(a). All samples showed a sharp increase in m-ZrO_2 phase fraction after the first 10 min of exposure. The largest increase was observed for the (1Y, 1Nd)-ZrO_2 ceramic, containing 95% m-ZrO_2 after 10 min of exposure. While the 2Y-ZrO_2 and (1Y, 2Nd)-ZrO_2 samples contained 55 and 39% of m-ZrO_2, respectively. Comparing the Y_2O_3 and mixed stabilised compositions separately, the monoclinic fraction decreased with increasing stabiliser content, indicating a higher stability of the metastable tetragonal phase. The 2Y-ZrO_2 sample, however, completely degraded after 20 min of testing, whereas the (1Y, 1Nd)-ZrO_2 ceramic was still intact. The latter one however degraded after 40 min of hydrothermal testing. The kinetics of the m-ZrO_2 phase formation showed a logarithmic behaviour, levelling off at elongated testing times. Comparing the curves of the 3Y- and (1Y, 2Nd)-ZrO_2, reveals that the m-ZrO_2 content on the surface increases faster and reaches a higher level for the co-stabilised grade, suggesting a higher hydrothermal stability for the yttria stabilised ceramic at the surface since the X-ray penetration depth is only a few micrometers. The 3Y-TZP grade however completely degraded after 1280 min, whereas the sample integrity of the co-stabilised grade was still intact, as shown in Fig. 3(b) and (c). This can only be explained by a reduced in-depth degradation of the double stabilised material.

4. Discussion

The mechanical properties of the Y- and (Y, Nd)-TZPs are summarized in Table 1. The transformability and concomitant toughness of the yttria-stabilised ceramics is modest due to the very short dwell time of 3 min at 1450 °C during PECS, limiting ZrO_2 grain growth. The transformability and toughness of the double stabilizer systems is substantially higher although the average grain size of the (1Y, 1Nd)-TZP is smaller than for the 2Y-TZP grade (see Fig. 2). The transformability and toughness decrease with increasing Nd_2O_3 co-stabilizer content.

The XRD patterns of the main tetragonal peak around 30.25° 2θ of the 2Y, 3Y, 1Y-1Nd and 1Y-2Nd grades are compared in Fig. 4, showing a shift to lower 2θ values, i.e. larger lattice parameters and lower tetragonality with increasing Nd_2O_3 content. Since the substitution of Y^{3+} by Nd^{3+} has no effect on the amount of oxygen vacancies in the lattice, the larger lattice parameters of the 1Y-1Nd and 1Y-2Nd grades have to be attributed to the larger ionic radius of Nd^{3+}, 0.1109 nm, compared to Y^{3+}, 0.1019 nm [14]. Since the XRD patterns were subsequently recorded, there is no influence of the experimental setup on the 2θ position.

In order to investigate how the substitution of Y^{3+} by Nd^{3+} influences the phase formation as well as the unit cell dimensions of ZrO_2 ceramics with the same overall stabiliser content, high temperature XRD experiments were conducted on 3Y and (1Y, 2Nd)-coated ZrO_2 powders. XRD scans were recorded during both heating and cooling with temperature intervals of 50 °C starting from 700 °C. Selected patterns for the 3Y-ZrO_2 and (1Y, 2Nd)-ZrO_2 ceramics during heating are shown in Fig. 5(a) and (b), respectively. It is clear that the t-ZrO_2 phase formation at 1050 °C is more pronounced in case of the Y_2O_3-stabilised system. Moreover, the intensity of the symmetrical (1 1 1) t-ZrO_2 peak increases quickly between 1050 and 1200 °C for the 3Y-ZrO_2 ceramic and remains at the same 2θ position, in agreement with an increasing dissolution of Y_2O_3. The initial t-ZrO_2 peak position in the co-stabilised material however is shifted to a substantially lower 2θ value compared to that of the 3 mol% yttria stabilised material, what could be correlated to the larger ionic radius of Nd^{3+} compared to Y^{3+}. The t-ZrO_2 peak evolves into an asymmetrical peak with a maximum shifting to higher 2θ values with increasing temperature. The reason for the asymmetry is not yet fully understood, but might be related to a competitive dissolution of the Y_2O_3 and Nd_2O_3 stabilisers that are initially present as a coating on the m-ZrO_2 starting powder.

Although the dissolution of the stabiliser in the yttria and co-stabilised systems is far from completed at 1200 °C, as illustrated in Fig. 6, the extent of t-ZrO_2 phase stabilisation at 1200 °C is higher for the Y_2O_3-stabilised system. This suggests that the dissolution of Nd^{3+} into ZrO_2 requires more time and/or a higher temperature than the dissolution of Y^{3+}. The cooling curves in Fig. 6 indicate that the t-ZrO_2 formed is metastable at room temperature since minimal t to m transformation is observed during cooling. The room temperature XRD patterns of the ceramic grades PECS at 1450 °C, shown in Fig. 4, reveal that the crystal lattice of the mixed (1Y, 2Nd)-ZrO_2 ceramic is slightly larger compared to the 3Y-ZrO_2 ceramic.

The thermo-mechanical dilatometer data on the 3Y, 1Y-1Nd and 1Y-2Nd grades are compared in Fig. 7. The 3Y-TZP grade shows

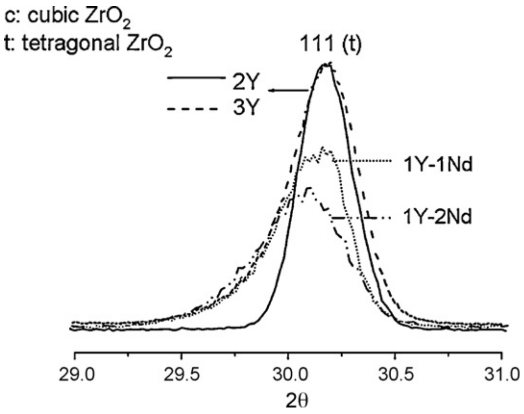

Fig. 4. Room temperature X-ray diffraction patterns of the (1 1 1) t-ZrO_2 peak of the PECS grades as a function of the stabiliser amount and type.

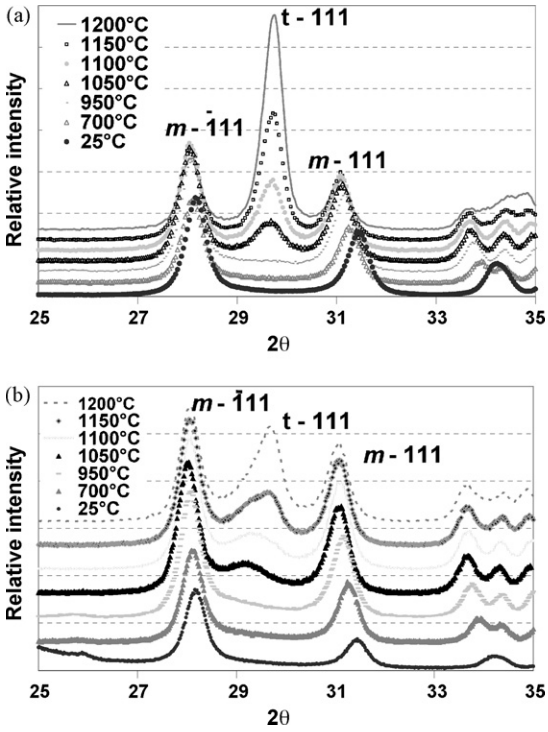

Fig. 5. Phase composition evolution of 3 mol% Y_2O_3 (a) and 1 mol% Y_2O_3 + 2 mol% Nd_2O_3 (b) coated m-ZrO_2 powder during heating up to 1200 °C.

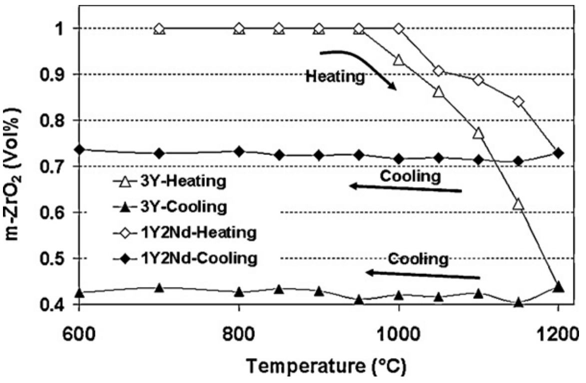

Fig. 6. Evolution of the m-ZrO_2 phase content of a 3 mol% Y_2O_3 (▲, △) and 1 mol% Y_2O_3 + 2 mol% Nd_2O_3 (♦, ◇) coated ZrO_2 powder compact during heating (open symbols) up to 1200 °C and subsequent cooling (filled symbols).

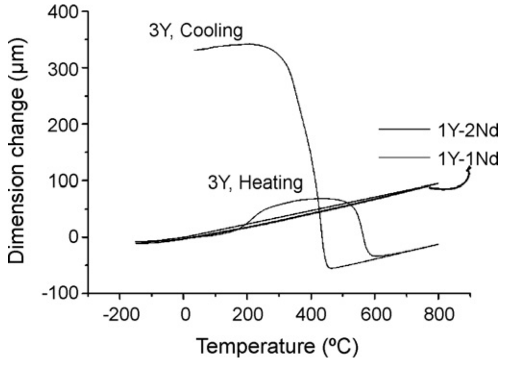

Fig. 7. Dilatometer data of the 3Y, 1Y-1Nd and 1Y-2Nd ceramics.

a volume expansion around 200 °C during heating, corresponding with a t to m phase transformation that should be attributed to LTD. The m-ZrO_2 phase is converted to t-ZrO_2 when heating above 500 °C. During cooling, the martensitic transformation is clearly observed with an A_s temperature around 450 °C. Despite the high transformability of the t-ZrO_2 phase (see Table 1), no phase transformations were observed for the 1Y-1Nd and 1Y-2Nd grades during thermal cycling to 800 °C, implying that the martensitic transformation in the double stabilizer grades is not thermally activated within the investigated temperature region. In other words the metastable T_0 (t/m) temperature, i.e. the temperature at which the chemical energy of the t- and m-ZrO_2 phase are equal, is lower for the mixed stabilizer systems, which is claimed to be a requirement for increasing resistance to LTD since this slows down the kinetics [4].

The prevailing explanation for LTD in literature is that moisture, in the form of OH^- or other species, diffuses into the zirconia lattice and fills oxygen vacancies, lowering the vacancy concentration and thereby destabilizing the tetragonal phase [7,15,16]. The inward diffusion of moisture species is claimed to generate tensile hydrostatic stresses in the grains that modifies the oxygen configuration around the Zr ions leading to a destabilised tetragonal phase [7]. Although the substitution of Y_2O_3 by Nd_2O_3 does not alter the amount of oxygen vacancies, the incorporation of a larger Nd^{4+} cation results in a slightly larger lattice (see Fig. 4). This wider crystal lattice can actually result in a reduced lattice strain and concomitantly lower tensile stress generation upon interdiffusion of moisture species, therefore resulting in a lower susceptibility to LTD. It has been reported in literature that although Y-TZP as well as Ce-TZP with a CeO_2 content <10 mol% exhibit aging-induced transformation, the addition of both CeO_2 and Y_2O_3 was similarly found to be beneficial to obtain hydrothermally stable (Ce, Y)-TZP's [17].

5. Conclusions

Fully dense (1Y, xNd)-ZrO_2 (x = 1–2 mol%) ceramics were processed using pulsed electric current sintering at 1450 °C for 3 min. Although co-stabilising of Y_2O_3 with Nd_2O_3 shifts the onset temperature of t-ZrO_2 phase formation to a higher temperature during sintering, the transformability of the t-ZrO_2 phase and the concomitant fracture toughness is substantially higher in case of co-stabilised TZP, despite the smaller grain size. The higher resistance of the mixed (Y, Nd)-ZrO_2 ceramics against hydrothermal degradation was attributed to the lower T_0 (t/m) temperature and the increased unit cell dimensions of the metastable tetragonal phase, making the material less susceptible to internal straining by moisture species diffusing into the crystal lattice.

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