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Composition design and mechanical properties of mixed (Ce,Y)-TZP ceramics obtained from coated starting powders

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Abstract

The microstructure and mechanical properties of a selection of ceramics with compositions in the low ceria and yttria corner of the ZrO_2–CeO_2–Y_2O_3 system were investigated and evaluated. The calculated isothermal section of the ZrO_2–CeO_2–Y_2O_3 system at 1450 °C was used to define the CeO_2 content range of interest resulting in an optimum amount of tetragonal ZrO_2 phase for TZP ceramics with an overall yttria content of 2 and 1 mol%. Pure monoclinic ZrO_2 starting powder was coated with the appropriate amount of yttria and ceria stabiliser by means of a suspension coating technique and pressureless sintered in air at 1450 °C. The indentation toughness and Vickers hardness were evaluated as a function of the sintering time, grain-size and stabiliser content. An excellent fracture toughness of 13–15 MPa $m^{1/2}$ was obtained for ZrO_2 ceramics with 1 mol% Y_2O_3 + 4 mol% CeO_2, sintered for 1–4 h at 1450 °C.

Keywords: ZrO_2; Sintering; Microstructure; Mechanical properties; Thermodynamics; TZP; Coatings

1. Introduction

Tetragonal zirconia polycrystals (TZP) exhibit excellent mechanical properties such as strength and fracture toughness.[1,2] The high toughness is due to the stress-induced martensitic transformation from the tetragonal (t-ZrO_2) to the monoclinic (m-ZrO_2) zirconia phase. Yttria-doped zirconia with 2–3 mol% Y_2O_3 exhibits a very high strength and fracture toughness. However, the mechanical properties of Y-TZP are greatly degraded by low temperature ageing at 200–300 °C in a humid atmosphere and hot aqueous solution.[3,4] The degradation is due to a spontaneous transformation from t-ZrO_2 to m-ZrO_2, accompanied by the formation of micro-cracks during ageing. On the other hand, CeO_2-stabilized TZP ceramics have a considerably higher hydrothermal stability than Y-TZP under similar conditions.[5,6] In the ZrO_2–CeO_2 system, stabilization of t-ZrO_2 occurs over a wide composition range from 12 to 20 mol% CeO_2, with a preferred composition of 12 mol% ceria.[6] Moreover, experimental investigations revealed that the hydrothermal stability of Y-TZP can be significantly improved by doping with a suitable amount of ceria.[7–9] A homogeneous dispersion of fine Al_2O_3 grains into a TZP matrix has been reported to suppress grain growth and increase the hardness, elastic modulus as well as the hydrothermal stability of the t-ZrO_2 phase.[10] Recently, it was found that the properties of Y-TZP/Al_2O_3 and Ce-TZP/Al_2O_3 composites obtained from yttria and ceria-coated zirconia powders are more attractive than those of co-precipitated powder based ceramics.[11–13]

In the present study, thermodynamic calculations were conducted to determine the stabiliser range in the ZrO_2–CeO_2–Y_2O_3 system at 1450 °C. After selecting the proper compositions, CeO_2 and Y_2O_3 co-stabilised zirconia

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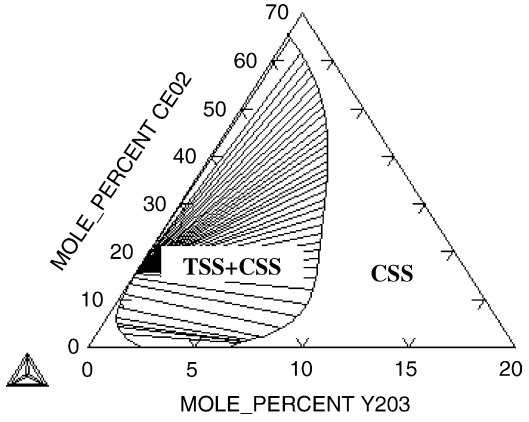

Fig. 1. Calculated partial phase diagram of the ZrO_2–Y_2O_3–CeO_2 system at 1450 °C.

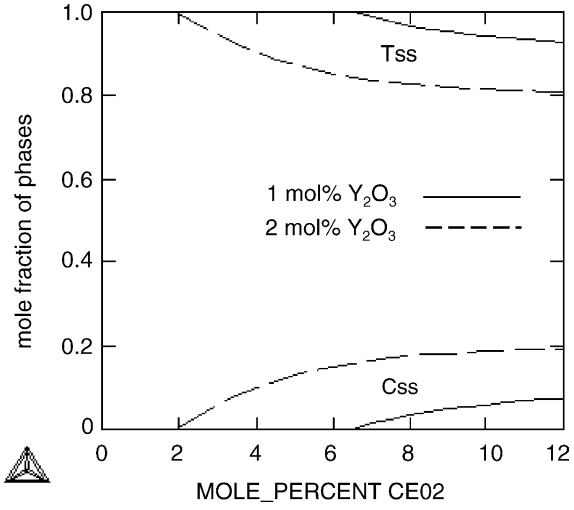

Fig. 2. Calculated Tss and Css phase content for 1 and 2 mol% Y_2O_3 co-stabilised (Y,Ce)-TZP ceramics as a function of the CeO_2 content at 1450 °C.

powders were synthesized by a colloidal coating technique and pressureless sintered in air. The influence of the stabiliser content and composition on the microstructure, grain-size, fracture toughness and hardness of the ceramics are investigated and evaluated.

2. Composition selection

Although some experimental findings in the ternary ZrO_2–CeO_2–Y_2O_3 system have been published,[3,4,7–9] no complete phase diagram of this system, especially on the relation between the tetragonal and cubic solid solution (Tss/Css) ratio and the overall composition has been reported. The isothermal section of the ZrO_2-rich corner of the ZrO_2–CeO_2–Y_2O_3 system at 1450 °C, extrapolated with the optimised thermodynamic data from Li et al.[14,15] using Thermo-Calc[16] is presented in Fig. 1. Fig. 2 shows the calculated Tss and Css phase relation for a 1 and 2 mol% Y_2O_3 stabilised (Y,Ce)-TZP as a function of the CeO_2 content up to 12 mol%. It is obvious that a lower stabiliser content corresponds to a higher Tss/Css ratio at 1450 °C. For example, a (2Y,4Ce)-TZP contains 9.8 mol% Css, whereas only 0.4 mol% Css is calculated for a (2Y,2Ce)-TZP at 1450 °C.

Based on the calculated phase relations, the CeO_2 stabiliser content for a 1 mol% Y_2O_3 stabilised material was varied from 2 to 8 mol%, whereas the CeO_2 content for a 2 mol% Y_2O_3 stabilised grade was varied from 0 to 4 mol%, in order to investigate fully tetragonal (1450 °C) as well as tetragonal ceramics with a small amount of cubic phase. The selected compositions and nomenclature of the different ceramic grades are summarized in Table 1.

3. Experimental procedure

Pure monoclinic ZrO_2 nanopowder (Tosoh grade TZ-0) was coated with the appropriate amount of yttria and ceria by means of a suspension coating technique.[11–13] The chemicals used are Y_2O_3 (grade YT-603, Atlantic equipment Engineers), cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Aldrich Chemical Company) and ethanol. $Y(NO_3)_3$ was prepared by the dissolution of Y_2O_3 in HNO_3 (65%). Al_2O_3 (2 wt.%) powder (grade SM8, Baikowski, 0.6 μm) was added to all powder mixture grades.

To break the agglomerates in the ZrO_2 starting powder, Y-TZP milling balls (Tosoh grade TZ-3Y) with a diameter

Table 1
Ceramic grades, composition, calculated Tss–Css phase content at 1450 °C, calculated T_0, the temperature at which the chemical energy of the t- and m-ZrO_2 phase are equal, and the calculated martensitic transformation temperature, M_s

Ceramic	CeO_2 (mol%)	Y_2O_3 (mol%)	Al_2O_3 (wt.%)	Tss (mol%)	Css (mol%)	T_0 (°C)	Grain-size[a] (μm)	M_s (°C)
2Y2Al	0	2	2	100	0	519	1.55	−16
2Y1Ce2Al	1	2	2	100	0	508	1.37	−20
2Y2Ce2Al	2	2	2	99.6	0.4	486	1.39	−25
2Y4Ce2Al	4	2	2	90.2	9.8	426	1.10	−64
1Y2Ce2Al	2	1	2	100	0	688	1.54	36
1Y4Ce2Al	4	1	2	100	0	629	1.38	11
1Y6Ce2Al	6	1	2	100	0	538	1.97	−2
1Y8Ce2Al	8	1	2	96.6	3.4	438	1.62	−54

[a] The maximum measured grain-size intercept, used for the M_s calculation.

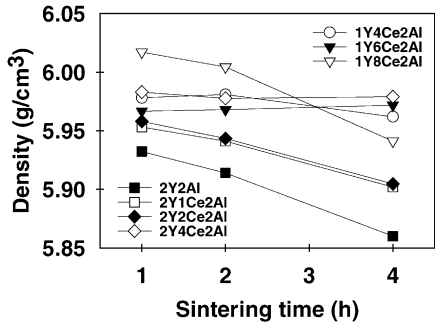

Fig. 3. Density of 2Y*x*Ce2Al and 1Y*x*Ce2Al ceramics as a function of CeO_2 content and sintering time at 1450 °C.

of 10 mm were added to the ethanol suspension containing cerium nitrate, yttrium nitrate and m-ZrO_2 nanopowder. To avoid contamination, mixing was performed in polyethylene containers. After mixing for 36 h on a multi-directional mixer (type Turbula), water and ethanol were removed from the suspension by a rotating evaporator at 95 °C. The dried powders were subsequently calcined in alumina crucibles in air at 800 °C for 1 h. Due to the relative hard nature of the calcined powder agglomerates, a similar second mixing process was performed in ethanol to obtain soft agglomerates. The soft powder agglomerates were shaped in small cylinders (Ø and L = 10 mm) by cold isostatic pressing (CIP) at 300 MPa for 3 min. Sintering was performed at 1450 °C for 1–4 h in a tube furnace under a dry air flow of 100 ml/min at a heating rate of 20 °C/min from 25 to 1000 °C and 10 °C/min from 1000 to 1450 °C. Cooling was performed at 20 °C/min.

The Archimedes technique was applied to measure the density (BP210S balance, Sartorius AG, Germany) of the samples in ethanol. Phase identification was carried out by X-ray diffraction (XRD, 3003-TT, Seifert, Ahrensburg, Germany) using Cu Kα radiation (40 kV, 30 mA). The XRD profiles were scanned in 0.02° step increments from 20° to 40° to determine the m-ZrO_2/(t + c)-ZrO_2 ratio. The as-sintered samples were thermally etched in air at 1350 °C for 30 min after polishing, and investigated by scanning electron microscopy (SEM, XL30-FEG, FEI, The Netherlands). The average grain-size was determined by IMAGE-PRO software according to the line intercept method[17] technique measuring about 1000 grains. The average grain-size data are presented as measured since no mathematical corrections were performed. The Vickers hardness HV_{30} was measured on a Zwick hardness tester with an indentation load of 30 kg. The indentation fracture toughness, K_{IC}, was obtained from the radial crack pattern of HV_{30} indentations, and the toughness was calculated according to the formula of Anstis et al.[18] using an elastic modulus of 200 GPa. The reported values are the mean and standard deviation of at least five indentations.

4. Results and discussion

The density of the 2Y*x*Ce2Al and 1Y*x*Ce2Al ceramics sintered at 1450 °C is presented as a function of the sintering time in Fig. 3, indicating that the density of most material grades gradually decreased with increasing sintering time. As revealed by XRD analysis on polished samples, the decreased density at longer sintering times should be attributed to the martensitic transformation of the t-ZrO_2 phase and the concomitant formation of microcracks. The 1Y4Ce2Al, 1Y6Ce2Al and 2Y4Ce2Al grades, however, remain fully tetragonal even after sintering for 4 h at 1450 °C. The appearance of a small amount of m-ZrO_2 in the diffraction pattern after longer sintering times is illustrated for the 2Y2Al

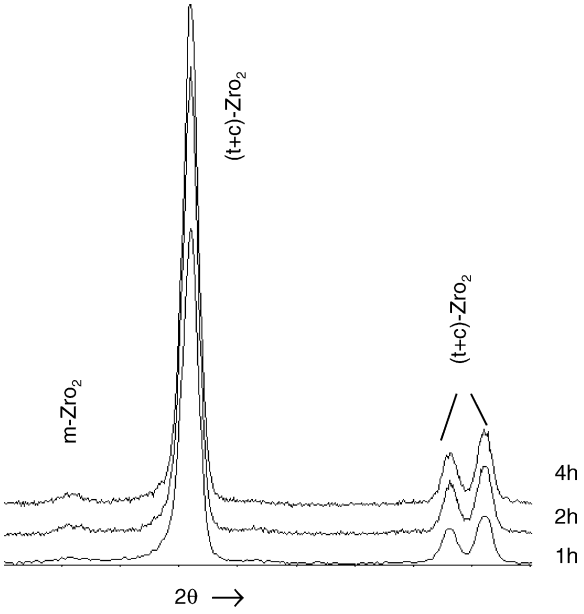

Fig. 4. XRD patterns for 2Y2Al sintered at 1450 °C for 1–4 h.

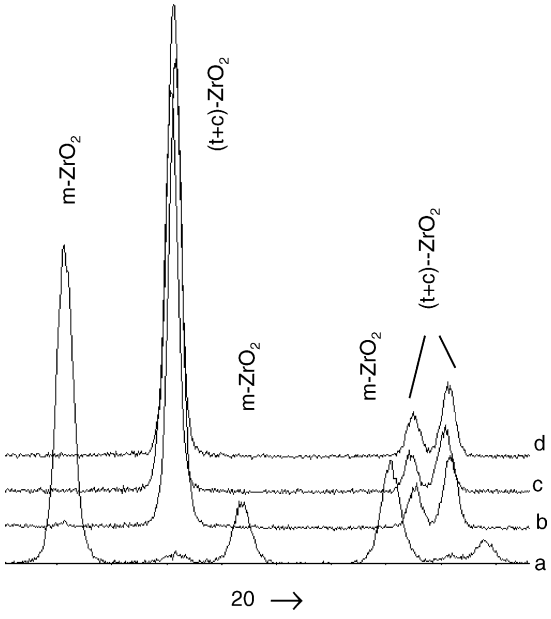

Fig. 5. XRD patterns of (1Y,*x*Ce)-TZP sintered for 1 h at 1450 °C, (a) 1Y2Ce2Al, (b) 1Y4Ce2Al, (c) 1Y6Ce2Al and (d) 1Y8Ce2Al.

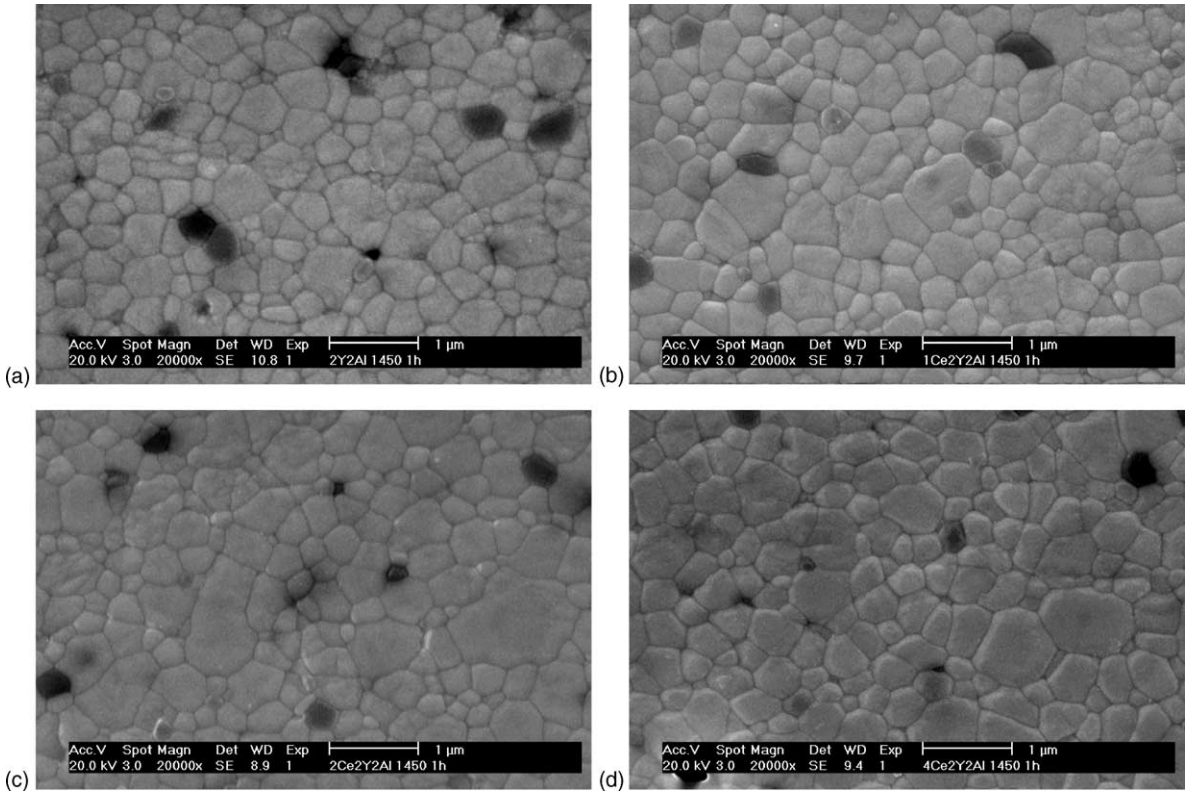

Fig. 6. SEM micrographs of thermally etched 2Y2Al (a), 2Y1Ce2Al (b), 2Y2Ce2Al (c) and 2Y4Ce2Al (d) ceramics sintered at 1450 °C for 1 h. The dark grains are Al_2O_3 particles.

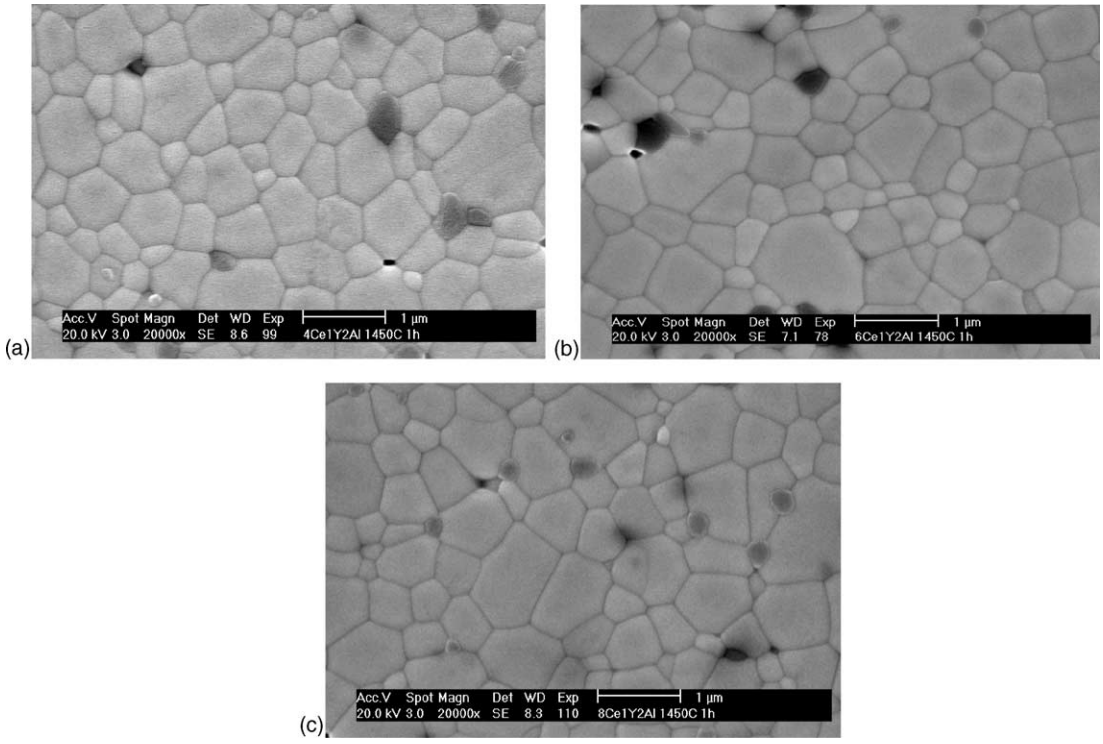

Fig. 7. SEM images for samples 1Y4Ce2Al (a), 1Y6Ce2Al (b) and 1Y8Ce2Al (c) sintered for 1 h at 1450 °C. The dark grains are Al_2O_3 particles.

material grade in Fig. 4. All investigated material grades, except 1Y2Ce2Al, are fully tetragonal after sintering for 1 h at 1450 °C, as presented in Fig. 5. It is obvious that the amount of stabilizer in the 1Y2Ce2Al ceramic is not enough to stabilize the t-ZrO_2 phase during cooling. However, the addition of more CeO_2, such as 4 mol% CeO_2 to a 1 mol% Y_2O_3 is sufficient to retain t-ZrO_2 at room temperature. Y_2O_3 (1 mol%) has never been reported to be enough to stabilize the tetragonal phase in a Y-TZP at room temperature.[20] It should, however, be mentioned that it is almost impossible to differentiate the Tss and Css phase by means of XRD, implying that the fully tetragonal samples might contain a minor amount of c-ZrO_2.

SEM micrographs of the thermally etched 2Y*x*Ce2Al and 1Y*x*Ce2Al material grades sintered for 1 h at 1450 °C are presented in Figs. 6 and 7. The dispersed alumina crystals, dark on the backscattered electron images, are pinned at the junctions of zirconia boundaries. The main microstructural difference between the 2Y*x*Ce2Al and 1Y*x*Ce2Al grades is the significantly smaller grain-size of the (2Y,*x*Ce)-TZP grades. As reported by Lange,[21] the grain-size of Y_2O_3-stabilised ZrO_2 decreases with increasing yttria content up to 2–3 mol%, and increases again with further yttria addition. Duh and Dai[7] found that a small addition of Y_2O_3 in Ce-TZP resulted in an effective grain-size refinement. It is well established that the stability of the metastable tetragonal zirconia phase is affected by several microstructural and compositional parameters including grain-size and morphology, stabilizer type and content and matrix constraint. The grain-size and stabilizer content are believed to be the most important amongst these parameters. It should be clear, however, that the ZrO_2 ceramics with an yttria content below 1.4 mol% were reported to be fully monoclinic,[21] whereas the additional stabilisation by CeO_2 in this work resulted in TZP ceramics. Fig. 8 presents the average grain-size of all investigated material grades as a function of the sintering time at 1450 °C. The grain-size of all material grades increases linearly with the sintering time. The grain-size of the (1Y,*x*Ce)-TZP and (2Y,*x*Ce)-TZP materials clearly increases with increasing CeO_2 addition especially for the lower Y_2O_3 content ceramics, as graphically illustrated for the 1Y4Ce2Al and 1Y8Ce2Al ceramics in Fig. 9.

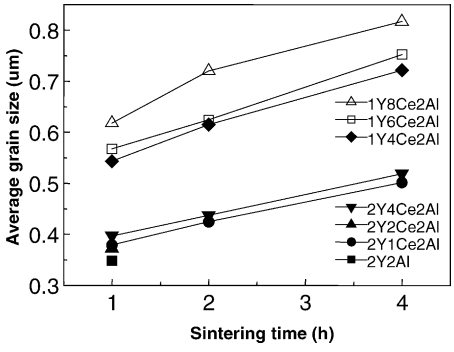

Fig. 8. Correlation of average grain-size and sintering time at 1450 °C.

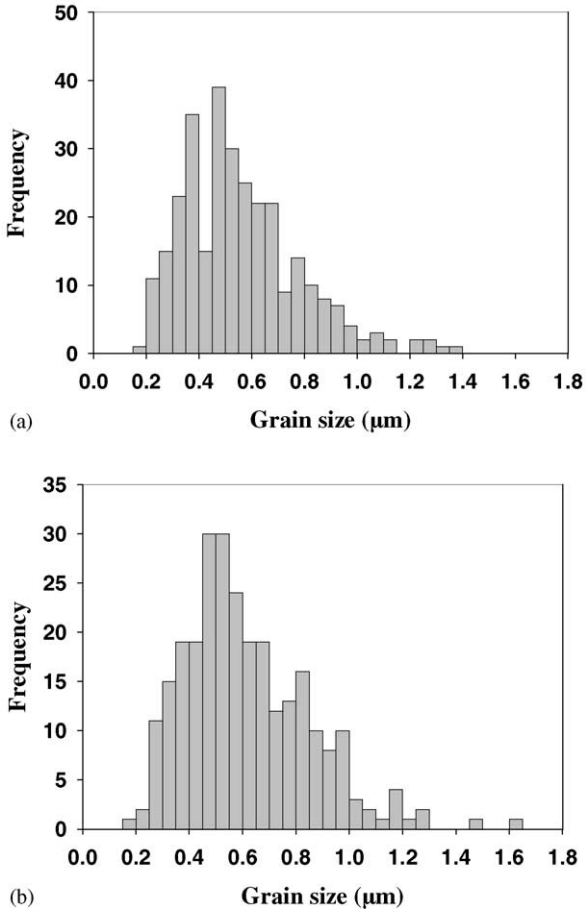

Fig. 9. Grain-size distribution of the 1Y4Ce2Al (a) and 1Y8Ce2Al (b) ceramics sintered for 1 h at 1450 °C.

Although no material grades without Al_2O_3 addition were investigated, it can be deduced from literature that the addition of small amounts of Al_2O_3 to a TZP matrix acts as a grain growth inhibitor and a sintering aid, enhancing densification during pressureless sintering and controlling the transformability and concomitant toughness of the material through tetragonal ZrO_2 grain-size control.[10,11]

To estimate the transformability of the t-ZrO_2 phase, the equilibrium temperature T_0, at which the chemical energy of the tetragonal and monoclinic phase are equal was calculated using Thermo-Calc.[16] The martensitic transformation temperature, M_s, of the samples sintered for 1 h at 1450 °C was calculated according to the formula reported by Zhang et al.[19] for the ZrO_2–CeO_2–Y_2O_3 system. The calculated T_0 and M_s of the selected compositions are summarized in Table 1. Since the martensitic transformation is enhanced in larger TZP grains, the largest measured grain-size intercept, listed in Table 1, was used in the calculation instead of the mean grain-size that was used in reference Zhang et al.[19] It is evident that the T_0 decreases with increasing CeO_2 and Y_2O_3 content. A higher T_0 results in a higher M_s temperature, representing a higher transformability of the t-ZrO_2 phase and concomitant increasing fracture toughness. These

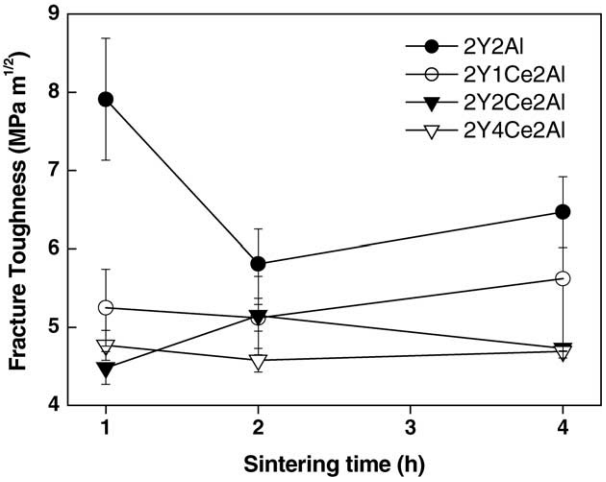

Fig. 10. Fracture toughness of the 2Y*x*Ce2Al as a function of the sintering time 1450 °C.

calculations allow the explanation of the relative ranking of the experimental toughness measured for the (2Y,*x*Ce)-TZP and (1Y,*x*Ce)-TZP ceramics, sintered for 1 h at 1450 °C.

The indentation toughness and hardness of the (2Y,*x*Ce)-TZP materials is graphically presented as a function of the sintering time at 1450 °C in Figs. 10 and 11. The highest toughness of 8 MPa $m^{1/2}$ was measured for the 2Y2Al ceramic after 1 h. The toughness, however, drastically decreased at longer sintering times due to spontaneous transformation of the t-ZrO_2 phase as presented in Fig. 4. The calculated T_0 and M_s of the 2Y2Al ceramic is higher than that of the other 2Y*x*Ce2Al ceramics, after 1 h of sintering at 1450 °C, explaining the higher toughness. The M_s temperature of 2Y2Al, is close to room temperature, implying that the transformation toughness of this material grade should be high, as confirmed by the toughness measurements (see Fig. 10). The fracture toughness of the (2Y,*x*Ce)-TZP grades with 1, 2 and 4 mol% CeO_2 is comparable, around 5 MPa $m^{1/2}$ and hardly influenced by the sintering time up to 4 h. Despite the fact that the grain-size increases with increasing CeO_2 addition (see Fig. 8), the hardness slightly increased with increasing CeO_2 content when sintering for 1 or 2 h at 1450 °C (see Fig. 11). The hardness trend amongst the samples sintered for 4 h as well as the evolution of the hardness as function of the sintering time is complex due to the interference of spontaneous transformation and the concomitant formation of microcracks.

The fracture toughness of the (1Y,8Ce)-TZP, plotted in Fig. 12, is comparable to that of the (2Y,*x*Ce)-TZP grades with 1, 2 and 4 mol% CeO_2, whereas the hardness, graphically presented in Fig. 13, is lower due to the significantly larger grain-size (see Fig. 8). The fracture toughness drastically increases with decreasing CeO_2 content in the (1Y,*x*Ce)-TZP grades, whereas the hardness decreases. The addition of 2 mol% CeO_2, however, is not enough to stabilise the TZP material, as illustrated by the spontaneous transformation of the 1Y2Ce2Al ceramic. The increased hardness with increasing CeO_2 addition is not so straightforward since the grain-size increases accordingly.

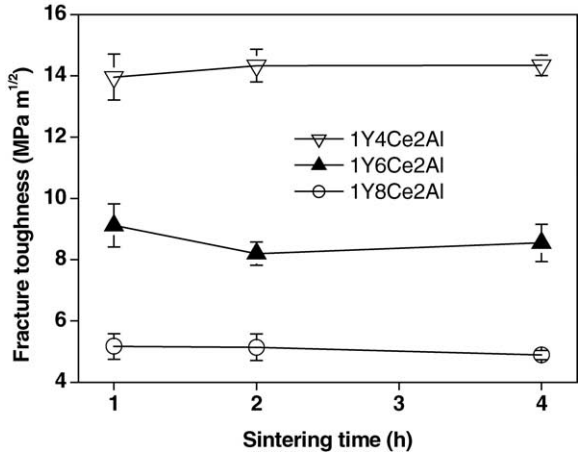

Fig. 12. Fracture toughness of the 1Y*x*Ce2Al as a function of the sintering time 1450 °C.

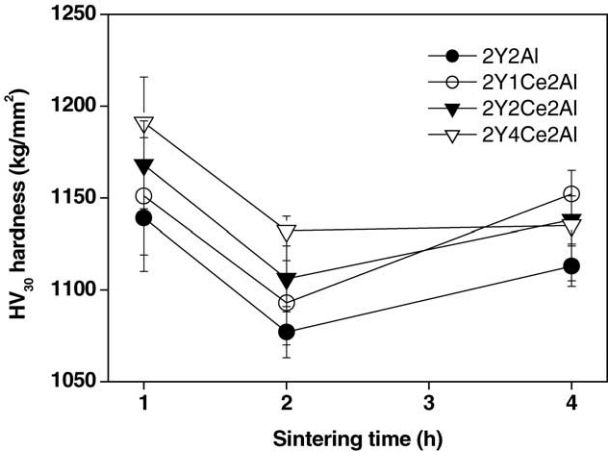

Fig. 11. Vickers hardness of the 2Y*x*Ce2Al ceramics as a function of the sintering time at 1450 °C.

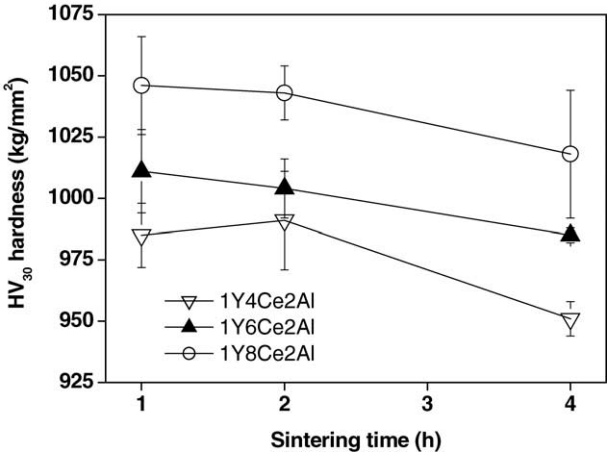

Fig. 13. Vickers hardness of the 1Y*x*Ce2Al ceramics as a function of the sintering time at 1450 °C.

An excellent toughness of 14 MPa $m^{1/2}$ was obtained for the 1Y4Ce2Al ceramic sintered for 1–4 h at 1450 °C. An acceptable toughness of 9 MPa $m^{1/2}$ was obtained for the 1Y6Ce2Al material, whereas the 1Y8Ce2Al grade has lower toughness of 5 MPa $m^{1/2}$. On the basis of thermodynamics, it is known that the transformability of these metastable materials increase with an increase in grain-size and a decrease in stabilizer content. The calculated T_0 and M_s of the 1Y*x*Ce2Al grades are listed in Table 1. The T_0 and M_s of the 1Y2Ce2Al grade is too high to retain all t-ZrO_2 at room temperature, resulting in spontaneous transformation as experimentally observed (see Fig. 5). The T_0 and M_s decrease with increasing CeO_2 content, explaining the decreasing transformability and concomitant toughness of the 1Y*x*Ce2Al grades.

The hardness of the 1Y*x*Ce2Al ceramics decreases with increasing sintering temperature, which correlates with an increase in grain-size. For a given sintering time, the hardness, however, also increases with increasing CeO_2 content, what cannot be directly related to the difference in grain-size (Fig. 3) or density (Fig. 8).

5. Conclusions

Fully tetragonal (1Y,4-8Ce)-TZP and (2Y,1–4Ce)-TZP ceramics could be obtained when sintering mixed stabilizer-coated monoclinic ZrO_2 nanopowders with the addition of 2 wt.% Al_2O_3 particles in air for 1–4 h at 1450 °C.

The grain-size of (1Y,*x*Ce)-TZP and (2Y,*x*Ce)-TZP ceramics increases linearly with the CeO_2 content and sintering time. The grain-size of the 2 mol% Y_2O_3 co-stabilised materials is significantly smaller than that of the 1 mol% Y_2O_3 stabilised ceramics.

The indentation toughness of the 2Y*x*Ce2Al ceramics with x = 1–4 mol% is comparable but lower than that of the 2 mol% Y_2O_3 stabilised material, whereas the hardness is higher. The toughness of the 1Y*x*Ce2Al ceramics is strongly influenced by the CeO_2 content. A minimum CeO_2 content of 4 mol% was needed to avoid spontaneous transformation, resulting in an excellent toughness of 14 MPa $m^{1/2}$. A respectable toughness of 8 MPa $m^{1/2}$ was obtained for the (1Y,6Ce)-TZP material whereas a modest toughness of 5 MPa $m^{1/2}$ was measured for the (1Y,8Ce)-TZP ceramic. The toughness of the (2Y,*x*Ce)-TZP ceramics with 1–4 mol% CeO_2 was comparable to that of the (1Y,8Ce)-TZP material. The hardness of (2Y,*x*Ce)-TZP, however, is higher than that of (1Y,*x*Ce)-TZP due to the smaller grain-size of the former.

Acknowledgements

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