

Characterization of a New Ternary Ce-Y-Tetragonal Zirconia

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Abstract

A new class of ternary tetragonal zirconia has been formed with cerium oxide (CeO_2) and yttrium oxide (Y_2O_3) additives. The fine grain microstructure of the sintered ceramic preserves the tetragonal phase down to room temperature and even below. The material has a high chemical homogeneity and presents an excellent resistance to steam corrosion together with reasonably good mechanical properties.

Eine neue Klasse eines ternären tetragonalen Zirkonoxids wurde unter Verwendung von Ceroxid (CeO_2) und Yttriumoxid (Y_2O_3) hergestellt. Die feinkörnige Mikrostruktur der gesinterten Keramik erhält die tetragonale Phase bis zur Raumtemperatur und tiefer. Das Material weist eine hohe chemische Homogenität und eine hervorragende Widerstandskraft gegen Wasserdampfkorrosion auf und hat zudem noch recht gute mechanische Eigenschaften.

Une nouvelle classe de zircone quadratique ternaire a été formée avec des additifs en oxyde de cérium (CeO_2) et d'yttrium (Y_2O_3). La fine granulométrie des céramiques frittées permet de préserver la structure quadratique à température ambiante et même en dessous. Le matériau a une grande homogénéité chimique et présente une excellente résistance à la corrosion par la vapeur d'eau ainsi que de raisonnablement bonnes propriétés mécaniques.

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Introduction

Interesting mechanical properties of yttrium doped tetragonal zirconia phase (Y-TZP) have promoted many research studies on this compound.¹ More recently there has been increasing interest in Ce-TZP phases for their higher steam corrosion resistance² and several recent papers have brought new insight into their mechanical properties associated with the martensitic transformation.^{3,4} In this context it was thought that one could perhaps obtain adjustable properties by alloying yttrium oxide (Y_2O_3) and cerium oxide (CeO_2) with zirconia.

The main objective of the present work was therefore threefold: (i) first to replace yttrium of the usual Y-TZP ceramic by a cheaper component; (ii) to lower or adjust to an optimal value the martensitic temperature of transformation⁵ which characterizes the transformability of the TZP phase;¹ and (iii) to improve the high temperature properties of TZP ceramics and decrease their hydrothermal degradation. A first attempt to replace yttrium was achieved previously with La_2O_3 .⁶ The tetragonal form of zirconia can be stabilized by La_2O_3 , but the evolution of the martensitic temperature with grain size⁷ does not presently permit densification, by conventional sintering, of an La-TZP ceramic. Other rare earths were thus tried and CeO_2 seemed promising when alloyed with Y_2O_3 . The second point was approached through the determination of the martensitic transformation temperature versus T for both Ce-TZP and Y-TZP.⁸ As the transformation is characterized by a hysteresis cycle, one

defines the martensitic start temperature (M_s) as the beginning of the transformation upon cooling; similarly A_s (austenitic start temperature) corresponds to the beginning of the transformation at heating. Only M_s has been used in the present work (as well as in Ref. 8). Knowledge of M_s was necessary in order to choose a proper composition in the ternary ZrO_2 - Y_2O_3 - CeO_2 system.

The methodology of our approach was first to fix the yttrium oxide content to 1 mole % and to screen over various CeO_2 concentrations to find a composition which permits the densification of a TZP ceramic with M_s at a temperature lower than room temperature. Simultaneously a method for detecting martensitic transformation below room temperature was developed⁹ and finally measurement of mechanical properties and evaluation of corrosion in hot steam were performed.

Experimental

The technique used to produce the various compositions essentially consisted in an impregnation of a fine pure ZrO_2 (99.99%) powder (CRICERAM, 38560 Voreppe, France). It was dispersed in distilled and demineralized water; the dopants were introduced as nitrates (99.9%) (Aldrich, Paris) ($Y(NO_3)_3$, $6H_2O$, $Ce(NO_3)_4$, $6H_2O$). After treating in a spray-dryer (Buchi, Roucaire, 78143 Velizy-Cédex, France), the powder was calcined at 600–700°C, which was enough to realize the solid solution. The powder was then deagglomerated in water with an ultraturax and then an ultrasonic probe, and finally dried in a vacuum desiccator. Up to 1000 g of product has been treated in this way. The powder was dry compacted isostatically (300 MPa) before sintering. The sintering was made at constant temperature; the optimal temperature was previously determined in a dilatometric study (SETARAM, Lyon, France) of the shrinkage versus temperature.

X-ray diffraction (XRD) (Philips goniometer, $Cu K\alpha$, Ni filtered) has been used to characterize the crystallographic structure of the phases. Microstructures were observed in a Cambridge Stereoscan 100 (CAMBRIDGE, Paris) by SEM and average grain size estimated from the line intercept method. An electron microprobe (CAMECA-CAMEBAX, BRGM, 45100 Orléans, France) has been used to evaluate the chemical homogeneity of the sintered Ce-Y-TZP. The M_s (and A_s) were determined by measuring the temperature of occurrence of the length anomalies on presintered samples ($d > 80\%$

d_{th}).⁶ DTA determinations were also made and agreed very well with the dilatometric characterization. For M_s smaller than room temperature a special spectroscopic technique was used.^{9,10} It consists of selectively exciting the Eu^{3+} fluorescence line, which is extremely sensitive to the site symmetry. The apparatus was operated at low temperature (77 K) and it is possible to detect with a high sensibility transformations below room temperature. The Eu is introduced at a low level (<0.3 mole %) on the zirconium site and is expected to have a negligible influence on the martensitic transformation.

Results and Discussion

Four preliminary CeO_2 doped compositions were elaborated containing $x=0, 1.3, 2.1$ and 3 mol % CeO_2 introduced in $(1-x)[ZrO_2-1 \text{ mol \% } Y_2O_3]$. After sintering for 2 h at 1450°C, fully dense ($d=6.25$) ceramics were obtained. The evolution of M_s (and A_s) with the CeO_2 content is displayed in Fig. 1. It may be compared with similar data concerning $ZrO_{2-x}Y_2O_3$ (Fig. 2). In this figure the black points (a–e) refer to experimental data obtained for several grain sizes (from 3 to 0.4 μm), the dashed line is only a guide line for the eyes, and the two heavy continuous lines are replotted from Andersson *et al.*,¹¹ giving, according to those authors, the limiting values for M_s versus T and x in $(1-x)ZrO_{2-x}Y_2O_3$ ceramics. The light continuous lines are the expected variations at constant grain size estimated from our results. Accordingly, M_s was found at 700°C for a $ZrO_2-1 \text{ mol \% } Y_2O_3$ ceramic composed of grains having a mean grain size of 1 μm . The introduction of 3 mol % CeO_2 decreases the M_s temperature down to 500°C for a 0.8 μm grain size ceramic.

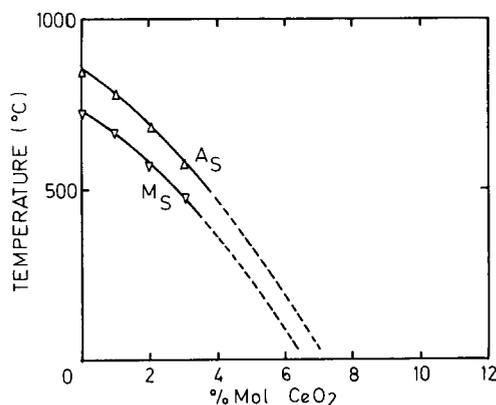


Fig. 1. M_s and A_s versus CeO_2 content in $(1-x)[ZrO_2-1 \text{ mol \% } Y_2O_3]_x CeO_2$ solid solution. M_s and A_s measure the temperature of the structural anomaly at the $T \rightarrow M$ transformation.

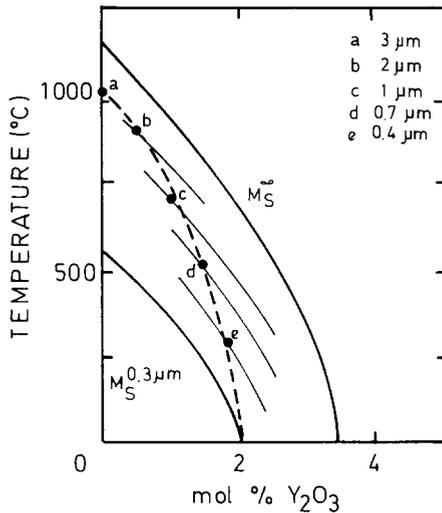


Fig. 2. M_s for $(1-x)\text{ZrO}_2-x\text{mol}\% \text{Y}_2\text{O}_3$. The black points (a–e) are for different grain sizes (3 to $0.4\ \mu\text{m}$). The dashed line is only a guide line for the eyes. The two heavy continuous lines are replotted from Andersson *et al.*¹¹ The light continuous lines are estimated variations at constant grain size.

Certainly, at constant grain size and yttrium content, the M_s is smaller for Ce-Y-TZP than for Y-TZP. This is a chemical effect that has not yet been studied extensively. By extrapolation of the M_s - T curve in Fig. 1, at constant grain size, one can expect M_s below room temperature for a CeO_2 content larger than 6 mol%.

The composition containing 1.3 mol% Y_2O_3 and 7 mol% CeO_2 was therefore synthesized by the previously described method and sintered in the same conditions. The powder is made of spheres having a small size dispersity (Fig. 3). The shrinkage (S) versus T was recorded and drawn in Fig. 4. The shrinkage behaviour is characteristic of a small

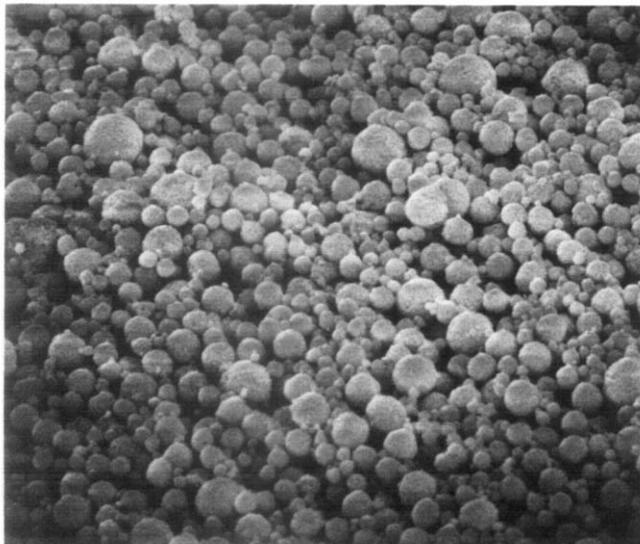


Fig. 3. Morphology of the dried powder: spheres with a mean size of $3\ \mu\text{m}$.

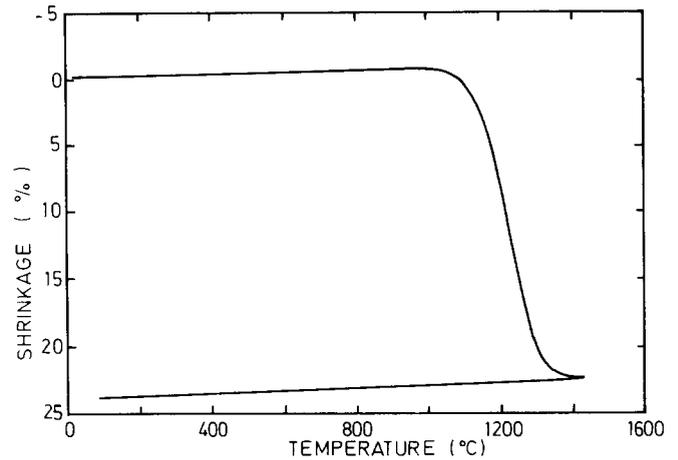


Fig. 4. Shrinkage versus T for the ternary Ce-Y-TZP 0.93 mol% $[\text{ZrO}_2-1.3\text{ mol}\% \text{Y}_2\text{O}_3]-7\text{ mol}\% \text{CeO}_2$ compacted at 300 MPa. The rate of temperature rise was $5\ \text{K min}^{-1}$.

dispersity in the agglomerate size,¹² traduced by only one maximum of the derived curve dS/dT . The total densification was achieved at 1450°C , and the grain size remained in the range of $0.8\ \mu\text{m}$ with a small dispersity (Fig. 5(a)). From the cooling part of the shrinkage curve (Fig. 2) it is obvious that no transformation of the martensitic type occurred down to 20°C . Accordingly, no trace of the monoclinic phase was detected by XRD (Fig. 6), even on fractured portions. The transformation into the monoclinic phase has been searched by site selective Eu^{3+} spectroscopy⁹ down to 77 K. *No trace of monoclinic phase* was visible, even with the high sensitivity of this method.

Chemical stability and homogeneity are expected to play a role in the retention of the metastable phase. These have been evaluated on that ternary phase before and after annealing at high temperature, i.e. 1700°C for 2 h. A normal grain growth to 2–3 μm was observed (no tendencies to de-densification) (Fig. 5(b)). This grain size remains below the critical grain size as the sample was still tetragonal at room temperature (Fig. 6). The chemical composition was also very homogeneous, as one can judge from the distribution of Y_2O_3 and CeO_2 among the sample as tested by electron microprobe

Table 1. Bending strength versus T of 0.93 mol% $[\text{ZrO}_2-1.3\text{ mol}\% \text{Y}_2\text{O}_3]-7\text{ mol}\% \text{CeO}_2$ sintered at 1450°C

T ($^\circ\text{C}$)	20	250	500	750
Bending strength (MPa)	600	370	200	160

Table 2. Bending strength at room temperature of steam-treated Ce-Y-TZP at various temperatures

T ($^\circ\text{C}$)	100	200	300
Bending strength (MPa)	470	530	400

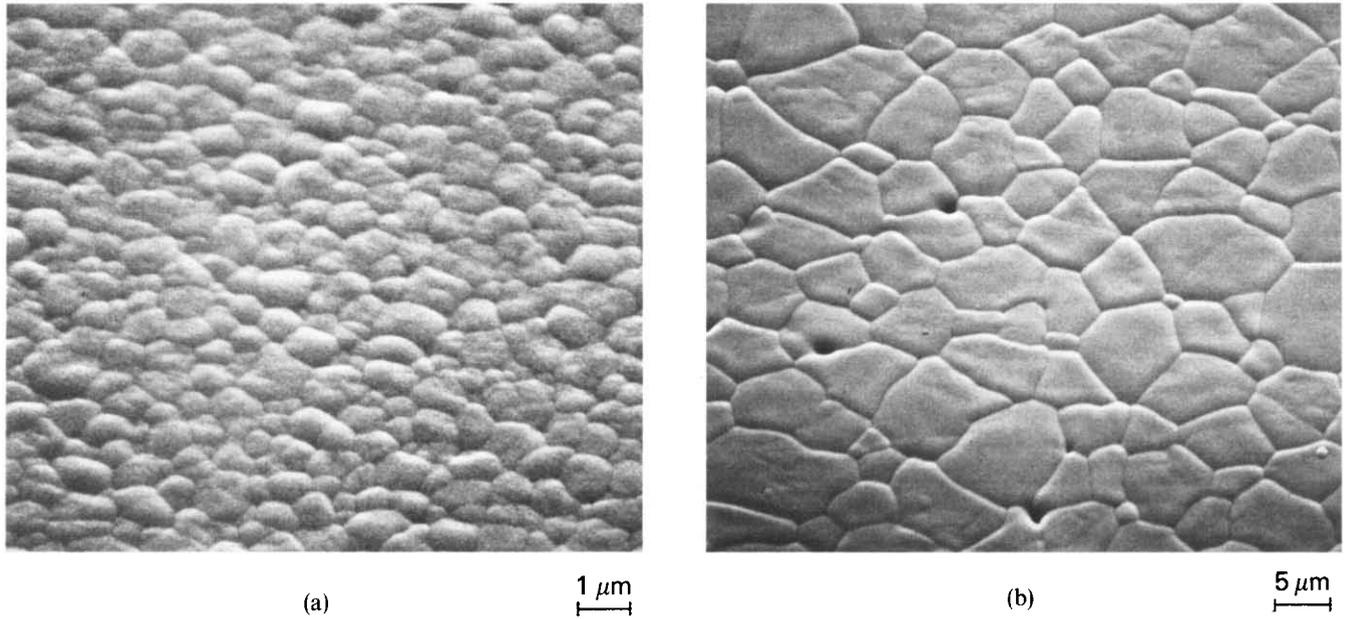


Fig. 5. Microstructure of the ternary Ce-Y-TZP 0.93 mol% [ZrO₂-1.3 mol% Y₂O₃]-7 mol% CeO₂ after sintering: (a) sintered at 1450°C for 2 h, the grain size is 0.8 μm on average; (b) the same after annealing at 1700°C for 2 h, grain size 2–3 μm.

(100 analysed points) (Fig. 7). Even the annealing at high temperature did not destroy the chemical homogeneity by phase separation or other phenomena. The thermal stability of this sample is therefore excellent.

Thirty-five specimens were cut (4 × 3 × 25 mm³) in

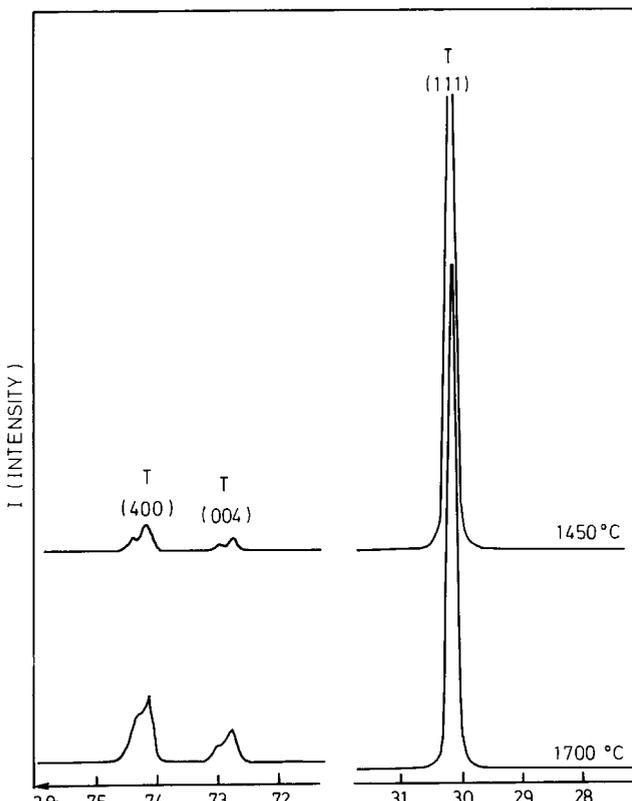


Fig. 6. XRD of the ternary 0.93 mol% [ZrO₂-1.3 mol% Y₂O₃]-7 mol% CeO₂. It is a pure tetragonal phase, i.e. $a = 0.5115 \pm 2 \times 10^{-4}$ nm, $c = 0.52101 \pm 2 \times 10^{-4}$ nm (monoclinic phase should have given reflection lines at 28° and 31.5° in 2θ).

the same sintered rod (at 1450°C) for three-point bending strength tests. Twenty of these were measured (with the ISO DIS 5013 standard at SFC Paris) for increasing temperatures, i.e. 250, 500 and 750°C. The 15 others were treated in H₂O steam at 100, 200 and 300°C during 2000 h and measured at room temperature. The samples measured at increasing temperatures follow the usual trend with a small decrease of the mechanical properties with T (Table 1). Toughness at room temperature was found in the range of 10 MPa m^{1/2}. The bending strength of

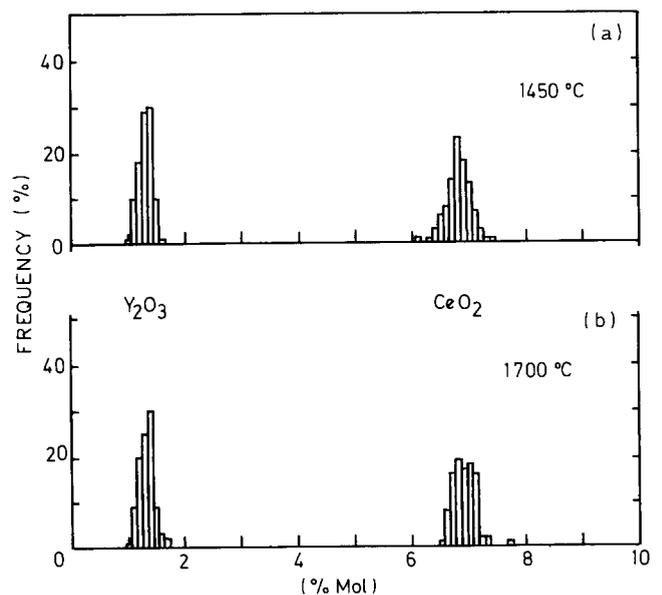


Fig. 7. Chemical homogeneity of the Ce-Y-TZP phase by electron microprobe: (a) as densified sample; (b) after further annealing at 1700°C for 2 h.

the steam-treated samples is still high, in the range of 500 MPa (Table 2), with a tendency to decrease for higher corrosion temperatures. It is therefore evident that this ternary composition is quite stable even under hot steam corrosion.

Conclusion

The present study brings new experimental data concerning the martensitic transformation temperature for Y-TZP and Ce-Y-TZP. Their general behaviour agrees well with the ideas developed several years ago by Andersson *et al.*¹¹ Plots of the inverse of grain size versus M_s ⁸ also agree with the predictions of Garvie and Goss.¹³

The above results show that the stability of Y-TZP (or Ce-TZP) phases can be controlled by Ce (or Y) alloying. Neither of the separated binary phases, i.e. 1.3 mol% Y-TZP nor 7 mol% Ce-TZP, could be prepared to be stable down to 77 K. Moreover, the chemical stability of the ternary Ce-Y-TZP is high and even stronger than that of Y-TZP. This is a benefit gained through the substitution of cerium and due to some extent to the equilibrium phase diagram constitution. The high stability at room temperature has been attributed for the similar Ce-Gd-TZP system¹⁴ to a crystal structure closer to that of the high temperature structure of the pure tetragonal form. It is interesting to emphasize that by site selective spectroscopy different types of tetragonal sites are observed in Ce-Y-TZP and Y-TZP.⁹ Finally, it should be underlined that the excellent stability against steam corrosion has been obtained, in this case, to the detriment of the mechanical strength at room temperature, which, however, only decreases from 1200–1300 MPa for Y-TZP to 600 MPa for the ternary Ce-Y-TZP.

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