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Influence of Dopant Content on Thermal Degradation of ZrO_2-CeO_2-Y_2O_3 Ceramics

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Abstract. Experiments to evaluate low temperature (200-300 °C) mechanical properties degradation of ZrO_2-CeO_2-Y_2O_3 ceramics in a humid atmosphere have been performed. Two sets of samples have been prepared: one with a 9 mol% ceria content and 1 to 4 mol% yttria additions; other with 2 mol% yttria content and 5.5, 7, 9 and 10 mol% ceria additions. The as-sintered pellets were characterized by X-ray diffraction and scanning electron microscopy (SEM). Apparent density was determined by the Archimedes method. Mechanical properties were evaluated by the Vickers indentation technique for the determination of hardness and fracture toughness. Some of the as-sintered specimens were annealed at 250 °C for 100 h in a water environment. The changes on microstructure, phase content and mechanical properties in aged specimens were evaluated and are discussed.

Introduction

It is well known Y_2O_3-stabilized tetragonal polycrystals (Y-TZP) possess excellent mechanical properties at high temperatures. However, the high strength and fracture toughness of this kind of TZP can be degraded by low temperature annealing in a humid atmosphere [1-3]. On the other hand CeO_2-stabilized tetragonal polycrystals (Ce-TZP) present higher fracture toughness and better thermal stability than Y-TZP. Nevertheless the strength of Ce-TZP is relatively low [4]. For this reason it has been proposed the development of ZrO_2-CeO_2-Y_2O_3 ceramics. The purpose of this study is the improvement of the mechanical strength of Ce-TZP and the thermal stability of Y-TZP.

This paper describes experiments that were conducted to evaluate the mechanical properties degradation of ZrO_2-CeO_2-Y_2O_3 ceramics at low temperatures (200-300°C) in a water environment. Mechanical properties degradation of zirconia ceramics is related to the spontaneous tetragonal to monoclinic phase transformation, which causes severe cracking of the ceramics. Several researchers have been investigated the ZrO_2-CeO_2-Y_2O_3 system [1, 5–12]. Duh and co-workers [5-10] have been concluded that ceria addition really avoids the tetragonal-monoclinic transformation and for that reason it is an efficient way to control mechanical properties degradation of yttria stabilized tetragonal zirconia polycrystals.

The aim of the present paper is to study the influence of ceria and yttria contents on thermal degradation behaviour of zirconia ceramics. Several compositions were investigated to optimize the development of zirconia ceramics which present high values of hardness and fracture toughness even after hydrothermal ageing at low temperatures.

Experimental Procedure

Powders were synthetized by co-precipitation method. The details of the processing and the synthesis methods are described on previous studies [13-17]. The chemical compositions of the powders are presented on Table 1.

Table 1: Chemical composition of the investigated powders.

sample code	composition (mol%) ZrO_2	CeO_2	Y_2O_3
1Y9Ce	90	9	1
2Y9Ce	89	9	2
3Y9Ce	88	9	3
4Y9Ce	87	9	4
2Y5Ce	92.5	5.5	2
2Y7Ce	91	7	2
2Y9Ce	89	9	2
2Y10Ce	88	10	2

The calcined powders were pressed uniaxially at 100 MPa and sintered at 1500°C for 1 h. The as-sintered pellets characterization was performed by X-Ray diffraction and scanning electron microscopy (SEM). Apparent density was determined by the Archimedes method. Mechanical properties were evaluated by Vickers indentation technique for the determination of hardness and fracture toughness values. It was used an indentation load of 50 N for all samples, except for 1Y9Ce where it was employed a load of 100 N to calculate fracture toughness. From the equation (1) the Vickers hardness is defined as [18]:

$$H_V = 1.8544 \times \frac{P}{d^2} \qquad \text{(eq.1)}$$

where H_v is the Vickers hardness (GPa);
P is the indentation load (N); and
d is the indent diagonal length (m).

To calculate fracture toughness it was employed the following equation developed by Shetty, Wright, Mincer and Clauer [19] for Palmqvist cracks:

$$K_{IC} = 0.0319 \times \frac{P}{a \times l^{\frac{1}{2}}} \qquad \text{(eq.2)}$$

where K_{IC} is the fracture toughness (MPa);
P is the indentation load (N);
a is the indent half-diagonal length (m); and
l is the crack length (m).

Hydrothermal ageing tests were performed in a stainless steel vessel with an internal PTFE container to evaluate the thermal degradation of ZrO_2–CeO_2–Y_2O_3 ceramics. Some of the as-sintered specimens were put in that container filled with distilled water. The specimens were annealed at 250°C for 100 h. The changes on microstructure, phase content and mechanical properties in aged specimens were evaluated by scanning electron microscopy, X - Ray diffraction and Vickers indentation method.

Results

The particle size distribution of the powders was performed by laser diffraction. The agglomerate mean size was at about 2 µm. The surface area values were determined by BET technique and were within the range 42 – 60 m^2 / g. X - Ray diffraction patterns showed the predominance of the tetragonal phase for all specimens. The density of as-sintered pellets and Vickers hardness and fracture toughness values, before and after the ageing test, are presented in Table 2 and 3 for the two sets of samples.

Table 2: Influence of yttria additions on density and Vickers hardness and fracture toughness values obtained before and after the hydrothermal ageing at 250°C for 100 h in a water environment.

sample code	ρ (g / cm³)	before ageing		after ageing	
		H_v (GPa)	K_{IC} (MPa)	H_v (GPa)	K_{IC} (MPa)
1Y9Ce	5.98 ± 0.03	9.48 ± 0.28	9.21 ± 0.91	-	-
2Y9Ce	6.00 ± 0.04	12.64 ± 0.18	5.09 ± 0.11	12.40 ± 0.16	4.85 ± 0.17
3Y9Ce	6.03 ± 0.05	12.91 ± 0.12	4.90 ± 0.08	12.47 ± 0.13	4.76 ± 0.05
4Y9Ce	5.94 ± 0.02	12.46 ± 0.18	4.22 ± 0.14	12.96 ± 0.13	4.63 ± 0.13

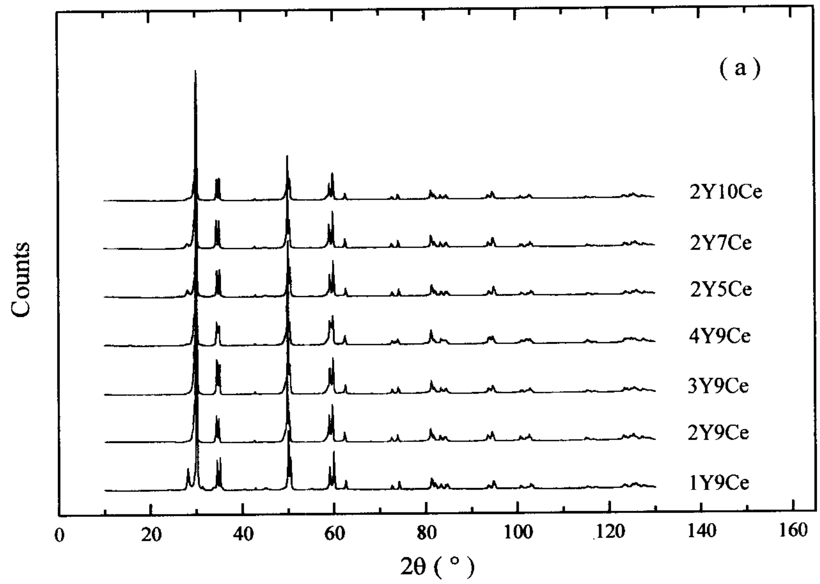
It has been observed that the density and Vickers hardness values increase as the yttria content increases. The scanning electron micrographs of the fracture surfaces showed an appreciable decreasing of grain size with the increasing of yttria content. Contrary to the Vickers hardness values behaviour, the fracture toughness decreases with the increasing of yttria additions. Lower density and consequently lower Vickers hardness value were reached for the specimen of zirconia doped with 4 mol% of yttria and 9 mol% of ceria, probably due to the presence of a small amount of cubic grains that leads to lower density. According to the phase diagram of ZrO_2-CeO_2-Y_2O_3 system this composition actually results in a mixture of tetragonal + cubic phase [20]. After the ageing tests no significant change on mechanical properties was verified, except for 1Y9Ce sample which its mechanical properties degraded completely. The dopant content was not sufficient to total stabilization of the tetragonal phase. There was an appreciable amount of monoclinic phase as observed in the X - Ray diffraction patterns of the as-sintered pellets.

Table 3: Influence of ceria additions on density and Vickers hardness and fracture toughness values obtained before and after the hydrothermal ageing at 250°C for 100 h in a water environment.

sample code	ρ (g / cm³)	before ageing		after ageing	
		H_v (GPa)	K_{IC} (MPa)	H_v (GPa)	K_{IC} (MPa)
2Y5Ce	6.06 ± 0.04	11.74 ± 0.12	7.01 ± 0.47	-	-
2Y7Ce	6.05 ± 0.05	11.84 ± 0.25	6.24 ± 0.52	12.31 ± 0.13	7.11 ± 0.48
2Y9Ce	6.00 ± 0.04	12.64 ± 0.18	5.09 ± 0.11	12.40 ± 0.16	4.85 ± 0.17
2Y10Ce	5.94 ± 0.02	11.89 ± 0.13	4.91 ± 0.08	12.45 ± 0.23	5.81 ± 0.18

With reference to ceria additions influence on mechanical properties of ZrO_2-CeO_2-Y_2O_3 ceramics, it has been noticed that the stability of the TZP increased when ceria content increases from 5.5 to 10 mol%. This behaviour could be explained by phase contents. The X - Ray diffraction patterns show a decreasing of the monoclinic phase content as ceria amount increases. The 5.5 mol% CeO_2-2 mol% Y_2O_3–ZrO_2 specimen presented the highest monoclinic phase content and collapsed after the hydrothermal test.

Fig. 1 (a) and 1 (b) show the X - Ray diffraction patterns of the pellets before and after the experiments performed to evaluate the mechanical properties degradation. There exists an intensive peak around $2\theta = 30^{\circ}$ which identifies the tetragonal phase. However there also exists a small peak at about $2\theta = 28^{\circ}$ which indicates the existence of small amount of monoclinic phase. As it has been already mentioned the monoclinic phase content decreases with the increasing of dopant content. It is important to notice that after the ageing the monoclinic phase content at the surface increased slightly for all samples. In addition, the fracture toughness increased for 2Y7Ce specimen probably due to the transformation toughening mechanism. In spite of the high monoclinic phase content mechanical properties were retained for this sample.



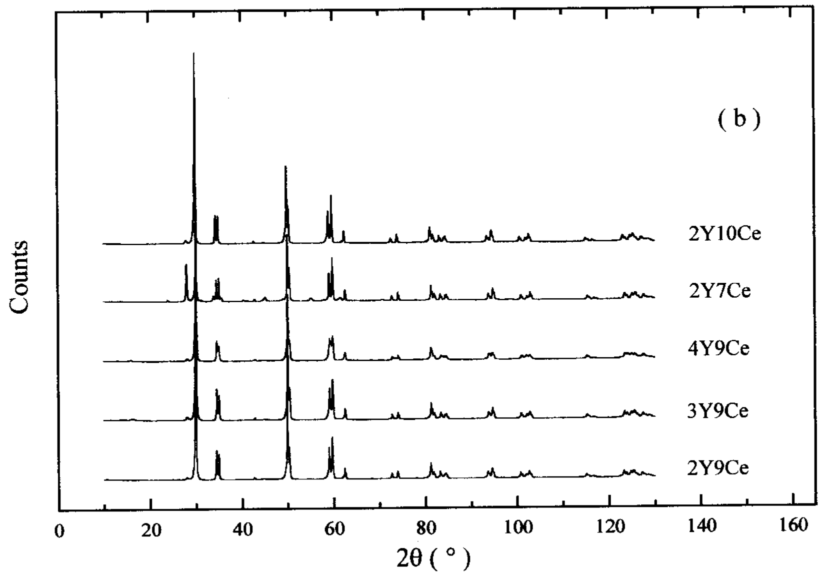
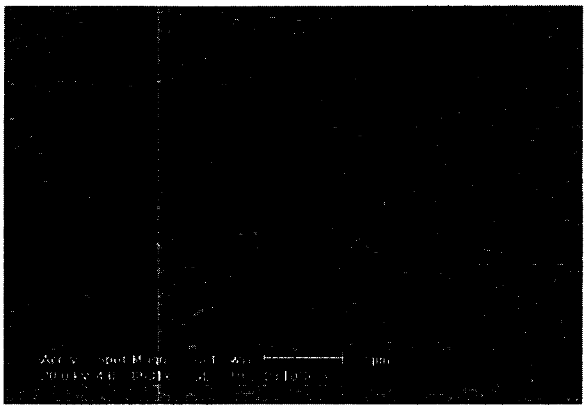
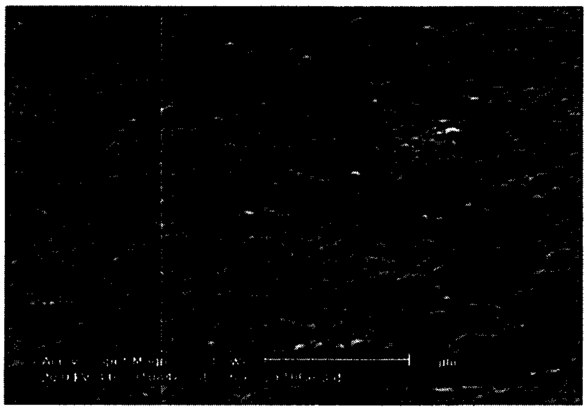


Figure 1: X – Ray diffraction patterns of as-sintered pellets (a) and for aged specimens (b).

As the mechanical properties were preserved, it has been supposed that the thermal degradation of the ceramics was only superficial. Fig. 2 shows the scanning electron micrographs of the surface of 2Y10Ce specimen before and after ageing. It can be observed that changes occurred on microstructure possibly due to the tetragonal to monoclinic phase transformation at the surface. This effect was similar for all samples and agreed with X – Ray diffraction results.



(a)



(b)

Figure 2: SEM micrographs of the surface for the 2Y10Ce sample: (a) before ageing and (b) after ageing.

Conclusions

Zirconia ceramics co-doped with ceria and yttria with good stability of tetragonal phase and good mechanical properties were obtained. Within the studied range, high dopant content causes better mechanical properties. The optimum composition for high Vickers hardness and fracture toughness values is 3 mol% Y_2O_3–9 mol% CeO_2–ZrO_2 with 12.91 GPa and 4.90 MPa respectively. Its mechanical properties are retained after the hydrothermal test at 250°C for 100 h.

The initial monoclinic content favours the thermal degradation. For this reason the aged 1Y9Ce and 2Y5Ce samples collapsed due to the tetragonal to monoclinic transformation which causes both microcracks and macrocracks. As it has been already discussed, the increasing of dopant amount increases the stability of t-phase.

Changes on monoclinic phase content and superficial microstructure are observed after ageing at 250°C for 100 h in a water environment for all specimens. This could be due to the tetragonal to monoclinic phase transformation at the surface that is confirmed by X – Ray diffraction patterns. The tetragonal phase transformed at the surface leads to fracture toughness increasing by transformation toughening mechanism. Studies will be subsequently performed to investigate the transformation depth.

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References

[1] M.T. Hernandez, J.R. Jurado, P. Duran, J. Am. Ceram. Soc. 74 (1991), p. 1254.
[2] S. Lawson, J. Eur. Ceram. Soc. 15 (1995), p. 485.
[3] T. Sato, M. Shimada, J. Am. Ceram. Soc. 68 (1985), p. 356.
[4] K. Tsukuma, M. Shimada, J. Mater. Sci. 20 (1985), p. 1178.
[5] J.G. Duh, H.T. Dai, B.S. Chiou, J. Am. Ceram. Soc. 71 (1988), p. 813.
[6] J.G. Duh, M.Y. Lee, J. Mater. Sci. 24 (1989), p. 4467.
[7] J.G. Duh, Y.S. Wu, J. Mater. Sci. Lett. 10 (1992), p. 1003.
[8] J.G. Duh, J.U. Wan, J. Mater. Sci. 27 (1992), p. 6197.
[9] J.U. Wan, J.G. Duh, J. Mater. Sci. Lett. 12 (1993), p. 575.
[10] J.D. Lin, J.G. Duh, J. Am. Ceram. Soc. 80 (1997), p. 92.
[11] M.M.R. Boutz, A.J.A. Winnubst, B. van Langerak, R.J.M. Olde Scholtenhuis, K. Kreuwel, A.J. Burggraaf, J. Mater. Sci. 30 (1995), p. 1854.
[12] S.R. Jansen, A.J. A. Winnubst, Y.J. He, H. Verweij, P.G.T. van der Varst, G. de With, J. Eur. Ceram. Soc. 18 (1998), p. 557.
[13] V. Ussui, F. Leitão, J.O.A. Paschoal, Proceedings of 39º Congresso Brasileiro de Cerâmica 3 (1994), p. 1151.
[14] V. Ussui, F. Menezes, C.A.B. Menezes, J.O.A. Paschoal, Proceedings of 39º Congresso Brasileiro de Cerâmica 1 (1994), p. 358.
[15] V. Ussui, D.R.R. Lazar, J.S.M. Nobre, S.M. Cunha, R.B. Ticianelli, F. Leitão, J.O.A. Paschoal, Proceedings of 11º CBECIMAT 2 (1995), p. 885.
[16] V. Ussui, D.R.R. Lazar, F. Menezes, C.A.B. Menezes, J.O.A. Paschoal, Cerâmica 42 (1996), p. 415.
[17] C.A.B. Menezes, D.R.R. Lazar, V. Ussui, J.O.A. Paschoal, Proceedings of 13º CBECIMAT (1998), file CESP 244 (CD-ROM), p. 3524.
[18] A. Iost, R. Bigot, J. Mater. Sci. 31 (1996), p. 3573.
[19] D.K. Shetty, P. Wright, A.H. Mincer, A.H. Clauer, J. Mater. Sci. 5 (1989), p. 865.
[20] Y. Hinatsu, T. Muromura, Mat. Res. Bull. 21 (1986), p. 1343-1349.

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