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The Role of Light Rare Earths in the Thermal Degradation Behaviour of ZrO_2-CeO_2-Y_2O_3 Ceramics

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Abstract. The objective of this paper is to evaluate the light rare earth influence on hydrothermal ageing behaviour of ZrO_2 – CeO_2 – Y_2O_3 ceramics at low temperatures (200 – 300 °C). With this purpose zirconia samples doped with 2 mol% of yttria and 10 mol% of light rare earth oxides were prepared using light rare earth concentrates. Powders were synthesized by the coprecipitation route. Apparent density values were determined by Archimedes method. The sintered pellets were characterized, before and after the ageing tests at 250 °C for 100 hours, by X – ray diffraction (Rietveld refinement), Vickers indentation technique, scanning electron microscopy and grain size determination. Results indicate that light rare earth presence has no significant effect on ZrO_2 – CeO_2 – Y_2O_3 ceramics performance. It was verified that the high purity oxides, that present high costs, are not required to obtain zirconia ceramics with better properties.

Introduction

Studies of the ZrO_2 – CeO_2 – Y_2O_3 system have been proposed to improve the tetragonal phase stability of the Y-TZP ceramics in humid atmosphere at low temperatures (200-300 °C). In these conditions the mechanical properties of these ceramics can be degraded due to the spontaneous tetragonal to monoclinic phase transformation [1-6].

Zirconia based-ceramics stabilized with ceria and yttria present good properties, such as thermal stability and high values of hardness and fracture toughness in the range of 10-12 GPa and 5-7 $MPa.m^{1/2}$, respectively [1-2, 4, 7]. Besides their applications as structural materials these ceramics show ionic and electronic conductivity at high temperatures in a reducing environment. Due to these good mechanical properties and the low resistivity this material can also be used, for instance, as solid electrolytes in solid oxide fuel cells and measuring and monitoring systems of oxygen [8-9]. However, as reported in the literature [1-4, 8-9], only high purity oxides have been employed to prepare the starting solutions, used in the coprecipitation processes. In this context it was verified that the use of light rare earth concentrates has to be evaluated, due to the cost reduction of the raw materials and consequently of the final product. Cerium, lanthanum, neodymium and praseodymium oxides constitute these concentrates.

In this context the purpose of the present paper is to study the influence of light rare earth concentrates on thermal degradation behaviour of zirconia – ceria – yttria ceramics. Results of the pellets characterization, before and after ageing tests, were compared for the samples prepared using the concentrates and the high purity oxides.

Experimental Procedure

Powders were synthesized by coprecipitation method. Details of the powder preparation and its characterization are described elsewhere [10]. Table I shows the molar composition and the code of the samples.

Table 1: Molar composition of the investigated samples.

sample code	light rare earth concentrate	composition (mol%)		
		ZrO_2	Y_2O_3	CeO_2 + RE oxide*
2Y10Ce-99	99 wt% CeO_2	88	2	10
2Y10Ce-98	prepared by fractional precipitation, 98 wt% CeO_2	88	2	10
2Y10Ce-90	prepared by fractional precipitation, 90 wt% CeO_2	88	2	10
2Y10Ce-La	synthetic mixture	88	2	10
2Y10Ce-Nd	synthetic mixture	88	2	10
2Y10Ce-Pr	synthetic mixture	88	2	10

* RE represents the light rare earth elements: lanthanum, neodymium or praseodymium.

To simulate the light rare earth concentrates, synthetic mixtures were prepared in order to provide 90 wt% of ceria and 10 wt% of lanthanum, neodymium or praseodymium oxides, respectively. Molar compositions of the light rare earth oxides in the studied samples are presented in Table 2.

Table 2: Molar composition of the light rare earth oxides in the ceramic powders, prepared from the synthetic mixtures.

sample code	composition (mol%)			
	CeO_2	La_2O_3	Nd_2O_3	Pr_6O_{11}
2Y10Ce-La	9.4	0.6	-	-
2Y10Ce-Nd	9.5	-	0.5	-
2Y10Ce-Pr	9.8	-	-	0.2

Calcined and ball-milled powders were pressed uniaxially at 100 MPa and sintered at 1500°C for 1 h. Before and after the ageing tests, the pellets were characterized by X-Ray diffraction, using the Rietveld method for the quantitative analysis of the phases and theoretical density determination; scanning electron microscopy (SEM) of the polished and thermally etched surfaces and grain size measurements. Apparent density was calculated by the Archimedes method. Mechanical properties were evaluated by Vickers indentation technique that provides the Vickers hardness and fracture toughness values. It was used an indentation load of 60 N. From the equation (1) the Vickers hardness is defined as [11]:

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

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 [12, 13] for Palmqvist cracks, typical for zirconia-based ceramics:

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

where K_{IC} is the fracture toughness ($MPa.m^{1/2}$);
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 the ceramics. Some of the as-sintered specimens were put in that container filled with distilled water and annealed at 250°C for 100 h.

Results

The particle size distribution of the powders, performed by sedimentation, showed that the samples are constituted by agglomerates in the range of 1 to 10 μm. The agglomerate mean size was at about 2 μm. The surface area values (BET technique) were within the range of 60-80 m^2 / g.
Table 3 presents the phase quantitative analysis, obtained by Rietveld refinement of the X-Ray diffraction patterns, of the as-sintered and aged pellets. It can be observed the predominance of tetragonal phase for all specimens. The use of light rare earth concentrates caused the increasing of the cubic phase amount (from 18 to 26 wt%). This behaviour occurred, probably, due to the formation of oxygen vacancies, originated from the doping with the trivalent cations, such as lanthanum, neodymium and praseodymium, in replacement of the Ce^{4+} ion. Considering the experimental errors of the method, it was assumed that no significant changes were verified after the ageing tests.

Table 3: Phase amount of the zirconia – yttria – light rare earth oxides, determined by Rietveld refinement of the X-Ray diffraction patterns, before and after the ageing tests.

sample code	phase amount (wt%)			
	before ageing		after ageing	
	tetragonal	cubic	tetragonal	cubic
2Y10Ce-99	81.6	18.4	79.5	20.5
2Y10Ce-98	79.1	20.8	75.0	25.0
2Y10Ce-90	73.4	26.6	74.2	25.8
2Y10Ce-La	79.6	20.4	79.8	20.2
2Y10Ce-Nd	80.4	19.6	81.7	18.3
2Y10Ce-Pr	73.6	26.4	77.5	22.5

Values of apparent, theoretical and relative density of the samples are presented in Table 4. High values of apparent density were achieved, resulting in relative densities in the range of 96-98% of the theoretical values. As it can be verified in the literature [14], the cubic phase density was lower than the tetragonal value. However, in this paper, the amount of the former phase wasn't enough to decrease the specimens density.

Table 4: Values of apparent, theoretical and relative density of the as-sintered pellets.

sample code	$\rho_{apparent}$ (g / cm^3)	$\rho_{theoretical}$ (g / cm^3)	$\%\rho_{theoretical}$
2Y10Ce-99	6.06 ± 0.02	6.24	97.1
2Y10Ce-98	6.00 ± 0.04	6.23	96.3
2Y10Ce-90	6.10 ± 0.04	6.22	98.1
2Y10Ce-La	6.05 ± 0.04	6.25	96.8
2Y10Ce-Nd	6.02 ± 0.01	6.25	96.3
2Y10Ce-Pr	6.07 ± 0.01	6.25	97.1

Table 5 shows the grain size, Vickers hardness and fracture toughness values of the zirconia-based ceramics, before and after the hydrothermal ageing. Mean grain size are in the range of 0.4 to 0.6 μm. Fine-grained microstructure leads to high Vickers hardness values (10-12 GPa). However, the relatively poor fracture toughness (4-5 MPa.m$^{1/2}$) of these nanocrystalline samples is, possibly, due to a diminished capacity to transformation toughen via the tetragonal to monoclinic transformation [15]. It was observed that the employment of the light rare earth concentrates had no effect on these parameters.

Table 5: Mean grain size, Vickers hardness and fracture toughness values of the investigated ceramics, before and after the hydrothermal ageing tests.

sample code	mean grain size (μm)		H_V (GPa)		K_{IC} (MPa.m$^{1/2}$)	
	before	**after**	**before**	**after**	**before**	**after**
2Y10Ce-99	0.63 ± 0.21	0.54 ± 0.21	10.1 ± 0.1	10.7 ± 0.1	5.3 ± 0.1	4.3 ± 0.1
2Y10Ce-98	0.46 ± 0.15	0.48 ± 0.17	11.8 ± 0.2	11.6 ± 0.1	4.9 ± 0.1	4.3 ± 0.1
2Y10Ce-90	0.43 ± 0.14	0.44 ± 0.15	11.6 ± 0.5	10.7 ± 0.2	4.5 ± 0.1	4.3 ± 0.1
2Y10Ce-La	0.43 ± 0.14	0.43 ± 0.14	11.0 ± 0.1	10.9 ± 0.1	5.0 ± 0.1	4.6 ± 0.1
2Y10Ce-Nd	0.40 ± 0.14	0.42 ± 0.14	10.1 ± 0.1	10.1 ± 0.1	5.2 ± 0.1	4.6 ± 0.1
2Y10Ce-Pr	0.41 ± 0.14	0.43 ± 0.16	11.0 ± 0.3	10.7 ± 0.1	4.9 ± 0.1	4.5 ± 0.1

Micrographs of the polished and thermally etched surfaces (Fig. 1), obtained by SEM, illustrate the typical microstructures of the prepared ceramics, which are constituted by nanometric grains, independently of the raw materials employed in the coprecipitation processes. In Fig. 1c and 1d, it can be observed some coarser grains of cubic phase. This behaviour agrees with X-Ray diffraction results, which showed that the cubic phase amount increases for the samples obtained from the light rare earth concentrates. No modifications on the surface of the aged samples (Fig. 1b and 1d) were detected, proving the efficiency of light rare earths on the tetragonal phase stability of zirconia ceramics at low temperatures in humid atmosphere.

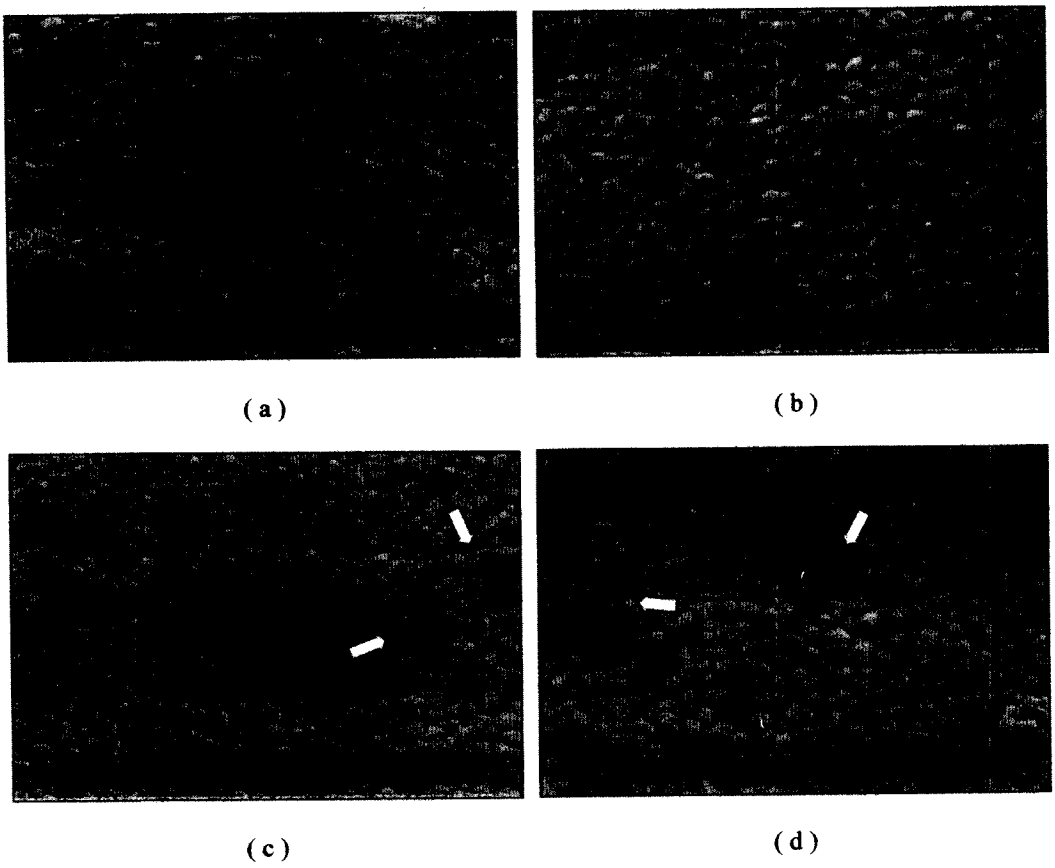

Fig. 1: Micrographs of the polished and thermally etched surfaces (SEM) of the samples 2Y10Ce-98 (a and b) and 2Y10Ce-Pr (c and d), before and after the ageing tests.

Conclusions

It was verified that the use of light rare earth concentrates, in replacement of high purity oxides, used as starting solutions in coprecipitation processes, allows the production of powders and ceramics with similar characteristics to those obtained from high purity oxides. For this reason it was confirmed that the use of high purity dopants, that present too high costs, are not necessary to obtain zirconia-based ceramics with better properties. No significant changes were observed on powder and as-sintered products (as a function of density, grain size and mechanical properties). This similar behaviour occurred probably due to the similar ionic radius of the light rare earths. With reference to the phases present in the ceramics, it was concluded that the addition of light rare earth oxides, such as lanthana, neodymia and praseodymia, has a higher tendency to stabilize the cubic structure of zirconia-based ceramics than cerium oxide. This effect is possibly due to the greater number of oxygen vacancies, caused by the trivalent ions. The small fraction of cubic grains avoids the thermal degradation at low temperatures in humid atmosphere, with no damage to the mechanical properties.
Zirconia ceramics stabilized with yttria and light rare earth oxides, that present good tetragonal stability, an important property for engineering ceramic materials, and good mechanical properties,

as a function of Vickers hardness (10-12 GPa) and fracture toughness (4-5 MPa.$m^{1/2}$), can be obtained. A fine-grained (0.4-0.6 μm) microstructure with low porosity (96-98% of the theoretical density) is observed for the investigated specimens.

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