MICROSTRUCTURAL INVESTIGATION OF PSZ SINTERED

IN LOW OXIGEN PARTIAL PRESSURE.

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Thermomechanical and electrical properties of zirconia-based ceramics have led to a wide range of advanced and engineering ceramic applications like solid electrolyte in oxigen sensors, fuel cells and furnace elements and its low thermal conductivity has allowed its use for thermal barrier coatings for aerospace engine components.

In this work, PSZ (partially stabilized zirconia) was studied to analyze the behavior during sintering in low oxygen partial pressure. The zirconia used was partially stabilized with yttria 8 wt%. The sintering temperatures used were 1600°C, 1700°C, 1800°C and 1900°C. The microstrutural investigation was done using Scanning Electron Microscope, X Ray Diffraction and density analysis.

The values of samples density showed that the increasing in sintering temperature was favorable to the material densification. The monoclinic phase converted in tetragonal and cubic phases. The tetragonal phase maintains constant in all sintering temperatures, but the cubic phase increased at 1700°C and 1800°C. The lattice parameters were calculated and showed similar in all sintering temperature.

Keywords: PSZ zirconia; sintering; densification.

Introduction

Pure zirconium oxide is an allotropic material and has a cubic structure from its melting point at 2680°C down to 2370°C, where it transforms to a tetragonal structure of similar cell size. Because of this small difference in crystalline cell volume, thermal cycling across the cubic-tetragonal transition temperature does not impose severe internal stresses. Following further cooling to below 1170°C, zirconia transforms to the monoclinic structure, which has about a 4% larger crystalline cell volume than the tetragonal structure [1]. Large internal stresses are generated as the transformation front sweeps through the material, which can lead to crack initiation. Commercially useful zirconia is alloyed with yttria, which has a cubic-plus-tetragonal two-phase field in its phase diagram (Fig.1) and inhibits the low-temperature tetragonal-to-monoclinic transformation [1, 2, 3].

Partially stabilized zirconia (PSZ) generally consisting of a cubic-ZrO_2 matrix with a dispersion tetragonal precipitates [5]. Specimens containing oxygen-deficient ZrO_2 have a very high affinity for oxygen and must be fired under conditions where the oxygen pressure is very low [6]. Partially stabilized zirconia, with about 6.5 to 9 wt% Y_2O_3, mostly avoids the monoclinic phase and the fully stabilized cubic-only phase, which is known to have less thermal shock resistance than the dual-phase cubic-plus-tetragonal structure [7].

A large cubic + tetragonal field exists which permits the formation of a partially stabilized zirconia (PSZ). Sintering is done at higher temperatures (up to 1700°C) to ensure tetragonal is taken into solution for the generation of fine, metastable tetragonal particles. The structures formed are complex. Under conditions of slow cooling from sintering and subsequent ageing, a diffusional reaction occurs giving tetragonal precipitates in a cubic matrix. The morphology of the tetragonal precipitates depends on the ageing temperature and time. However, with rapid cooling a displacive transformation occurs forming another

tetragonal phase, t', which has a lower c/a ratio than the normal tetragonal and contains the same quantity of yttria as the cubic [8].

Transformation toughening in ZrO_2-containing ceramics requires the presence of metastable tetragonal (t') zirconia, so that toughening obtainable from the stress-induced martensitic transformation to monoclinic (m) symmetry can be realized. When this type of ceramics is sintered in oxygen-deficient conditions, transformable cubic (c) phase appears, as a result of nonstoichiometry of ZrO_2 [9].

Experimental

The ZrO_2 powder used was produced and calcined (900ºC for 2 h) by Instituto de Pesquisas Energéticas (IPEN) with 97,5% of purity. The Y_2O_3 powder used had 99,6% of purity. The mixture of 8%wt of Y_2O_3 was made in a planetary ball mill. After, the powder was compacted in samples of 8 g in a steel die with internal diameter of 20 mm using a uniaxial hydraulic press Carver. To improve the densification, the samples was compacted in na isostatic press Paul Weber, with compaction speed of 15 MPa/s till a pressure of 250 MPa. The ceramic samples were sintered in vacuum of 10^{-7} Pa in a Thermal Technology Inc. furnace. The sintering temperatures used were 1600°C, 1700°C, 1800°C and 1900°C during 30 min. The microstructural investigation was done using Scanning Electron Microscope (SEM), X Ray Diffraction (XRD) and density analysis.

The ZrO_2 + 8wt% Y_2O_3 samples were prepared using usual metallography methods. To the grain boundary and porosity development used acid attack with phosphoric acid 85% at 250°C [10].

Results and Discussion

The relative density used a methodology based in Archimedes principle that considers the air relative density [11]; it used the value of 6,05 g.cm^{-3} to the Y-PSZ [8].

The value of relative density for a green ZrO_2 + Y_2O_3 tip was 50,13%. Fig. 2 shows the values of relative density to the different sintering temperatures. The increasing of sintering temperature is favorable to the material densification.

Fig. 3 shows the values of linear shrinkage to the different sintering temperatures. The linear contraction depends of the sintering temperature.

Fig. 4 to 5 shows the X ray diffraction of the ZrO_2 powder and of the ZrO_2 + Y_2O_3 sintering samples, respectively. The identification of phases present in ZrO_2 was done using JCPDS files [12] n° 13-307 to monoclinic phase, 17-923 to tetragonal phase and 27-997 to cubic phase. The quantity analysis of present phases in ZrO_2 based ceramics is so important to the study of phase's transformation tetragonal (t) – monoclinic (m) and its relation with material hardening [13]. In this method is used the ratio between the reflection intensities of three crystalline phases present (tetragonal, cubic and monoclinic). Then, is possible to obtain the molar fraction of the material phases through the X Ray Diffraction using equations suggested by Robert Miller [7]:

$$\frac{M}{T+C} = 0,82 \frac{I(11\bar{1})m + I(111)m}{I(111)t + c} \qquad \text{(Eq.1)}$$

$$\frac{C}{T} = 0,88 \frac{I(400)c}{I(400)t + I(004)t} \qquad \text{(Eq.2)}$$

$$M + T + C' = 1.00 \qquad \text{(Eq.3)}$$

where M, T, and C denote the mole percentages of the monoclinic, tetragonal and cubic phases, respectively, and *I(hkl)* is the integrated intensity for the (hkl) diffraction peak. From the peaks identification correspond to present phases of ceramic samples it's possible to calculate the molar fraction of monoclinic (M), tetragonal (T) and cubic (C) phase. Table I shows the phase contents and lattice parameters of ceramic samples sintering at 1600, 1700, 1800 e 1900ºC in vacuum. The phase content of monoclinic phase (M) was decreased with the sintering temperature, it was waited because the ZrO_2-Y_2O_3 phase diagram, Fig. 1, shows that in sintering temperatures used the monoclinic phase converts in tetragonal and cubic phases. Maybe if the samples had stayed for more time in sintering temperature, the monoclinic phase had converted completely in tetragonal and cubic phases. Another hypothesis is that the grain size of microstructure was large and hindering the conversion step of monoclinic phase to tetragonal and cubic phases. The tetragonal phase maintains constant in all sintering temperatures, but the cubic phase increased at 1700°C and 1800°C. The lattice parameters were calculated and showed similar in all sintering temperature.

Fig. 6 shows micrographies of ceramic samples obtained by SEM. The acid attack revealed the grain boundary and the porosity. The increasing of temperature was favorable to the densification through of the decreasing of the porosity.

Conclusions

The values of samples density showed that the increasing in sintering temperature was favorable to the material densification. The values of molar fraction of monoclinic phase decreased when the sintering temperature increased. The monoclinic phase converted in tetragonal and cubic phases. The tetragonal phase maintains constant in all sintering temperatures, but the cubic phase increased at 1700°C and 1800°C. The lattice parameters

were calculated and showed similar in all sintering temperature.

Acknowledgements

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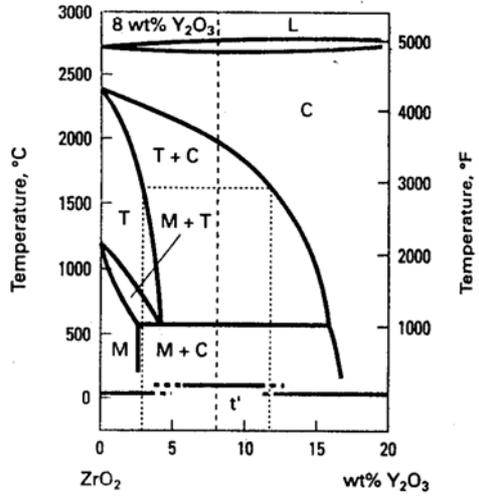[13] Nono, M.C.A. *Tese de Doutorado*, ITA, S. J. Campos, p.50, 1990.

Fig.1 – Phase diagram of the ZrO$_2$-rich region of the ZrO$_2$-Y$_2$O$_3$ system [4].
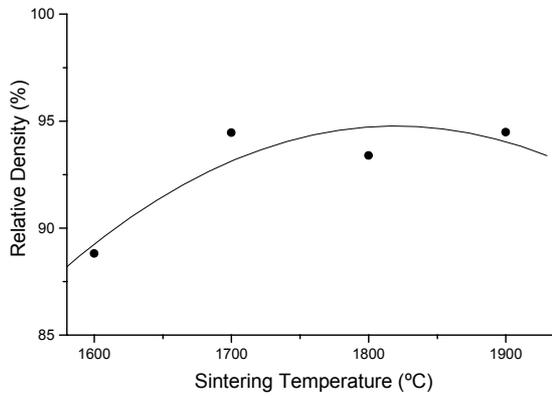

Fig.2 – Values of relative density obtained for different sintering temperatures.
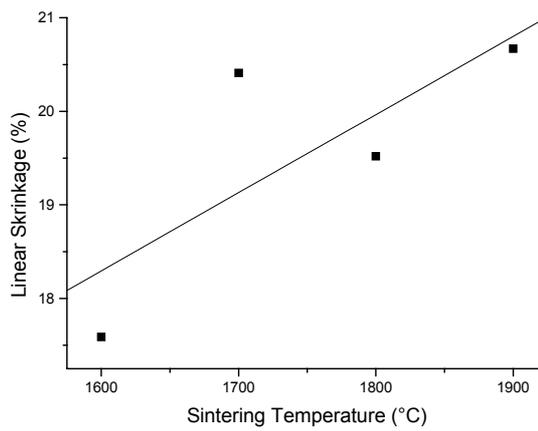

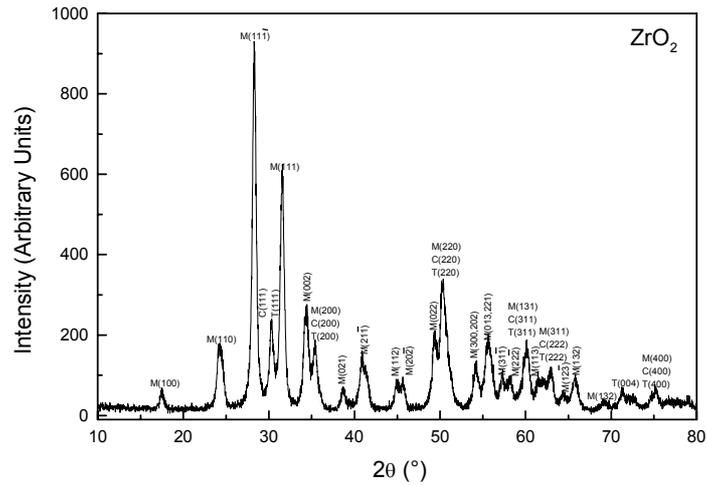Fig.3 – Values of linear shrinkage for different sintering temperatures.

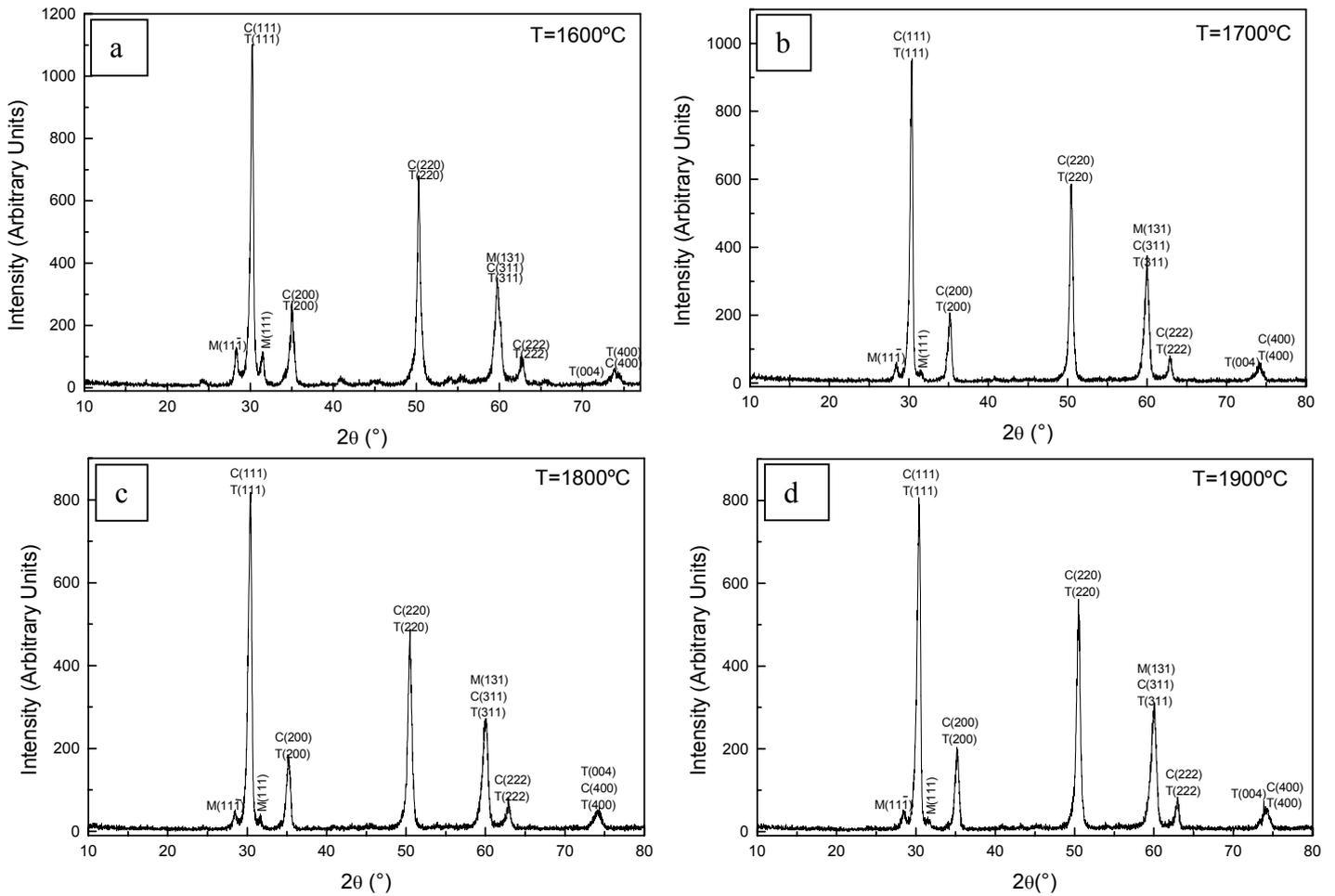Fig. 4 – X Ray Diffraction obtained for ZrO$_2$ powder.

Fig.5 – X Ray Diffraction obtained for ZrO$_2$ + Y$_2$O$_3$ samples sintered at

a) 1600°C, b) 1700°C, c) 1800°C and d) 1900°C.

Table I – Phase contents and lattice parameters of sintering samples.

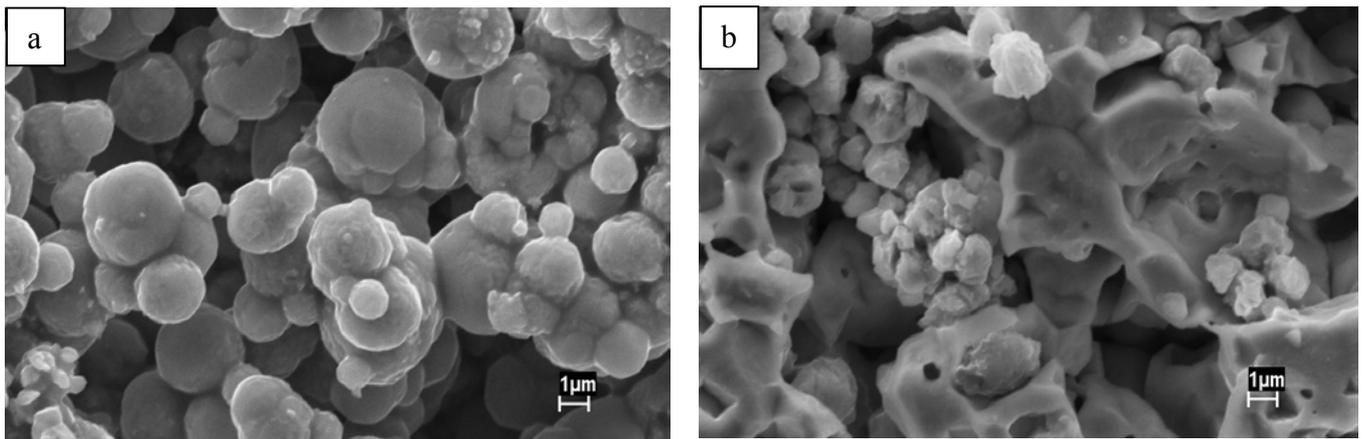| Sample	Phase (mol %)			Family Planes		Lattice Parameters		
						Tetragonal		Cubic
	M	T	C	{111}	{004}	a (Å)	c (Å)	a (Å)
1600°C	15,53	55,85	28,62	30,21°	71,61°	5,05	5,27	5,12
1700°C	8,05	50,80	41,15	30,41°	71,69°	5,01	5,26	5,09
1800°C	8,60	50,81	40,59	30,37°	71,63°	5,01	5,26	5,10
1900°C	8,21	58,57	33,22	30,37°	71,85°	5,02	5,25	5,10

Fig.6 – Micrographies of ZrO_2-Y_2O_3 samples sintered obtained by MEV:

a) 1600°C and b) 1800°C