EFFECT OF THE DIFFERENT SINTERING ATMOSPHERES ON THE STRUCTURAL CHARACTERISTICS OF THE PARTIALLY STABILIZED ZIRCONIA DOPED WITH 8wt%Y$_2$O$_3$

D.A.P. Reis[1*]; D.S. Almeida[2]; C.R.M. Silva[1,3]; M.C.A. Nono[4]; F. Piorino Neto[2]; M.J.R. Barboza[5]; C. Santos[5]

[1] *Instituto Tecnológico de Aeronáutica, ITA, São José dos Campos, Brazil.*
[2] *Comando-Geral de Tecnologia Aeroespacial, IAE, São José dos Campos, Brazil.*
[3] *Universidade de Brasília, UNB, Brasília, Brazil.*
[4] *Instituto Nacional de Pesquisas Espaciais, INPE, São José dos Campos, Brazil.*
[5] *Escola de Engenharia de Lorena, EEL-USP, DEMAR, Lorena, Brazil*

ABSTRACT

Thermo-mechanical and electrical properties of zirconia-based ceramics have led to a wide range of advanced and engineering applications like solid electrolyte in oxygen sensors, fuel cells and its low thermal conductivity has allowed its use for thermal barrier coatings for aerospace engine components. In this study, the effect of the sintering atmosphere in the in-situ stabilization of the Cubic- and Tetragonal-ZrO$_2$ phases were studied in ZrO$_2$-8wt.%Y$_2$O$_3$ ceramics. Powder mixture was compacted by cold isostatic pressing and sintered at 1600°C-30 minutes, in air and under vacuum. Sintered samples were characterized by relative density, X-ray diffraction and Scanning Electron Microscopy. Ceramics with relative density near to 90% were obtained in both sintering atmospheres and the sintering in air demonstrate an increasing of the cubic+tetragonal-ZrO2 stabilization, reducing the martensitic (T-M) transformation after sintering. In this form, a lower monoclinic is formed and consequently, a few higher densification was obtained in samples sintered in air. The lattice parameters of the tetragonal and cubic phases were determined to be similar and its proportion (65% and 35% respectively for ZrO$_2$-8wt.%Y$_2$O$_3$) is no influenced by the sintering atmosphere.

1. INTRODUCTION

Yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) are structural ceramics widely used for structural applications due to its mechanical properties, such as high fracture toughness and bending strength [1]. The use of ZrO$_2$ as advanced ceramic started in the 1970'ies, and since then a continuous improvement of these materials in various applications can be noted. The more promising applications of these are as structural ceramics (parts of implants, cutting tools, toughened ceramic) and as solid electrolytes (oxygen sensors, fuel cells). Pure undoped ZrO$_2$ exhibits the following phase transformations [1]:

$$monoclinic(m) \underset{950\,°C}{\overset{1170\,°C}{\leftrightarrow}} tetragonal(t) \overset{2370\,°C}{\longrightarrow} cubic(c) \overset{2680\,°C}{\longrightarrow} liquid$$
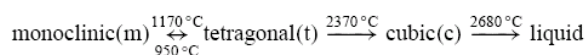
The transformations between different polymorphs are important for the processing and mechanical properties (strength, toughness, etc.) of zirconia ceramics. It has been well documented in the literature [1-2] that the t → m transformation in pure undoped zirconia during cooling is a reversible athermal martensitic transformation, associated with a finite amount of volumetric change (3–6%). Due to high volumetric expansion, associated to t-m transformation during the cooling, pure zirconia does not present practical applicability as an engineering material.

The addition of stabilizer oxides is indispensable to keep polymorphic phases of high temperatures in room temperature. Several dopants (Y$_2$O$_3$, CeO$_2$, MgO, etc.) are usually added to stabilize the high temperature tetragonal- and/or cubic-phase in the sintered microstructure [2]. Among these additives, yttrium oxide (Y$_2$O$_3$) is showed as the most usual stabilizer for ZrO$_2$ tetragonal phase, which is known as hard and extremely toughened phase at room temperatures making possible the use of this material at structural applications and in application like cutting tolls [1].

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 [3-6].

Partially stabilized zirconia (PSZ) generally consisting of a cubic-ZrO$_2$ matrix with a dispersed tetragonal precipitates [7]. Specimens containing oxygen-deficient ZrO$_2$ have a very high affinity for oxygen [8]. Partially stabilized zirconia, with about 6.5 to 9 wt% Y$_2$O$_3$, it 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 [9].

A large cubic + tetragonal field exists which permits the formation of a partially stabilized zirconia (PSZ). Sintering is done at high temperatures (up to 1700°C) to ensure tetragonal structure is taken into solution for the generation of fine, metastable tetragonal particles. The structures formed

* danielireis@hotmail.com

are complex. Under conditions of slow cooling from sintering and subsequent ageing, a diffusional reaction occurs, leading 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 (T) ZrO_2-phase, which has a lower c/a ratio than the normal Tetragonal and contains the same quantity of yttria as the Cubic-ZrO_2 [10].

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 non-stoichiometry of ZrO_2 [11].
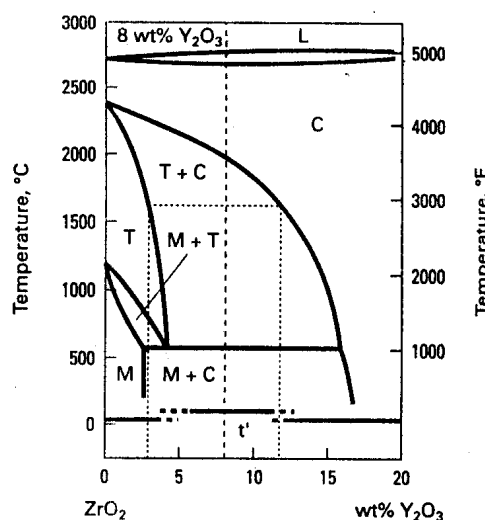

Figure 1 – Phase diagram of the ZrO_2-rich region of the ZrO_2-Y_2O_3 system [6].

In this study, the incorporation of the 8wt.%Y_2O_3 In the ZrO_2-matrix structure by sintering under different atmospheres was investigated. Sintered samples were characterized and compared as function of microstructure and Cubic- and Tetragonal- phase content.

2. MATERIALS AND METHODS

2.1 Processing

As starting powders, calcined ZrO_2 powder (IPEN-S.Paulo-Brazil)-97.5% of purity and high-purity Y_2O_3 (Grade, H.C.Starck-Germany) were used. A powder mixture containing 92 wt.% of ZrO_2 and 8wt.% of Y_2O_3 was prepared by milling using a planetary ball mill for 2h in isopropyl alcohol, using Al_2O_3 balls as medium, aiming the obtaining of Partially Stabilized Zirconia (PSZ) ceramic. After milling, the powder mixture was dried at 90^oC for 24 hours and deagglomerated. Cylindrical samples of 20mm of diameter were obtained by cold-uniaxial pressing under 80MPa pres-

sure. To improvement of the green density, the samples were cold-isostatic pressed, under 250MPa, resulting in samples with 51% of theoretical density.

The ceramic samples were sintered in air and under vacuum (10-7 Pa), using a $MoSi_2$ furnace at 1600^oC, for 30 min, with controlled heating- and cooling-rate of $10^oC/min$.

2.2 Characterization

The density after sintering was measured by the immersion method in distilled water, using Archimedes' principle [10] and relative density was determined correlating of the theoretical density of the ZrO_2-8%wt.Y_2O_4 (6.05g.cm^{-3}) [12]. Furthermore, linear shrinkage was measured comparing dimensions before and after sintering process.

Crystalline phase analysis was done by X-ray diffractometry using Cu-k α radiation in the 2θ range of 10 to 80°, with a step width of 0.05° and 2s of exposure time per position. The lattice parameters were determined using Trieste 1.0. Software.

Microstructure of the Y-PSZ sintered samples was examined by scanning electron microscopy (SEM): For microstructural characterization, polished samples were chemical-thermal etched using a phosphoric acid solution (85%) at 250^oC-15min [13].

3. RESULTS AND DISCUSSIONS

Table 1 shows the result of the relative density and linear shrinkage, as function of the sintering atmosphere used. The results indicate a little difference on the relative density, with an increasing of the densification as function of the use of the air as furnace atmosphere. Furthermore, the samples sintered in vacuum showed dark color because the oxygen deficit. A higher densification resulting of the sintering in air, promotes a subsequent increasing of the shrinkage.

Table 1 – Values of relative density obtained to the ZrO_2-8wt% Y_2O_3 samples sintering at 1600^oC, under different sintering atmospheres.

Sintering atmosphere	Relative Density (%)	Linear Shrinkage (%)
vacuum	88.8 ± 0.4	16.7 ± 0.4
air	93,7± 0.3	17.6 ± 0.5

Figures 2 to 4 shows the X ray diffraction pattern of the ZrO_2 powder and of the ZrO_2-8wt.%Y_2O_3 samples sintered in vacuum and in air, respectively. The identification of phases present in ZrO_2 and crystallographic planes, was done using JCPDS files [14,15] n° 13-307 (monoclinic phase), 17-923 (tetragonal phase) and 27-997 (cubic phase). In both cases (vacuum and air) observed the same phases converted. The starting powder is composed mainly of monoclinic-ZrO_2 and presents a residual tetragonal and cubic-ZrO_2 content. After sintering, independently of the sintering atmosphere, Cubic and tetragonal ZrO_2 phases are predominant.
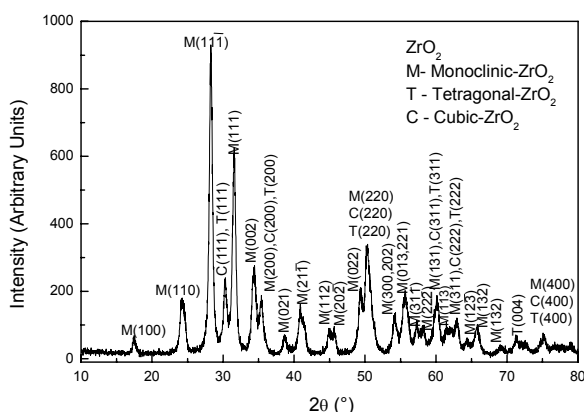
Figure 2 – XRD patterns of the ZrO₂ starting powder (M-Monoclinic ZrO₂; T – Tetragonal ZrO₂ and C – Cubic ZrO₂).
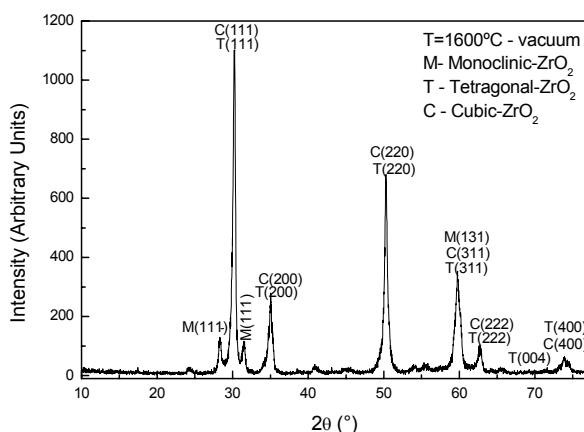

Figure 3 - XRD patterns of the ZrO₂-8wt.%Y₂O₃ samples sintered at 1600°C under vacuum. (M- Monoclinic-ZrO₂; T-Tetragonal-ZrO₂ and C-Cubic-ZrO₂).
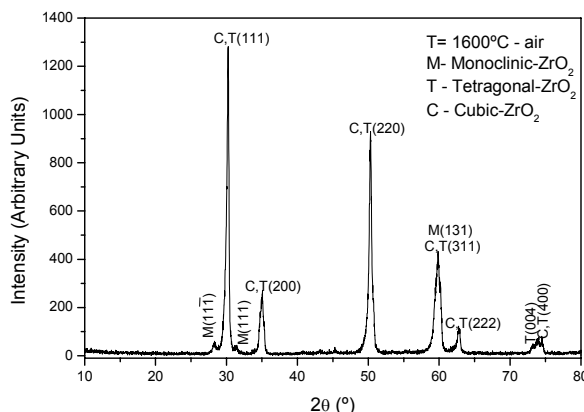

Figure 4 - XRD patterns of the ZrO₂-8wt.%Y₂O₃ samples sintered at 1600°C in air. (M- Monoclinic-ZrO₂; T – Tetragonal-ZrO₂ and C – Cubic-ZrO₂).

Aiming the determination of the effect of the sintering atmosphere on the cubic and tetragonal-ZrO₂ stabilization at room temperature after sintering, quantitative analysis of the

ZrO₂-Phases was evaluated. In this method is used the ratio between the reflection intensities of three crystalline phases present (tetragonal, cubic and monoclinic). Then, it is possible to obtain the molar fraction of the material phases through the X Ray Diffraction using equations suggested by Robert Miller [9]:

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

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

$$M + T + C = 1.00 \tag{3}$$

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 plane peak. From the peaks identification corresponds to present phases of ceramic samples it's possible to calculate the molar fraction of monoclinic (M), tetragonal (T) and cubic (C) phase.

Table 2 shows the phase contents and lattice parameters of ceramic samples sintered at 1600ºC in vacuum and in air.

Table 2 – Phase contents and lattice parameters of sintered samples.

Sample	Phase (mol %)			Family Planes		Lattice Parameters		
						Tetragonal		Cubic
	M	T	C	{111}	{004}	a (Å)	c (Å)	a (Å)
vacuum	15.53	55.85	28.62	30.21	71.61	5.05	5.27	5.12
air	8.21	53.62	33.16	30.21	73.21	5.09	5.17	5.12

The lattice parameters of the tetragonal and cubic crystalline phases of the sintered samples showed almost similar values in both, vacuum and air atmosphere. The lattice formations proposed by the incorporation to the Y-ions in the interstitial structure are similar because total Y₂O₃ was incorporated in the ZrO₂ structure during sintering.

Tomaszewski and Godwod [16] studied the influence of oxygen content in sintering atmosphere of undoped zirconia dispersed in alumina matrix and concluded that in the case of ceramics sintered in atmospheres with oxygen partial pressure between 2.80 X 10⁻⁵ Pa and 2.80 X 10⁻² Pa, 100% of zirconia is in the cubic form. The appearance of transformable c-ZrO₂ is a result of oxygen vacancy equal 9% seems to be the critical minimum value for this phase. Decreasing the oxygen vacancy concentration, as a result of increasing the oxygen content in the sintering atmosphere, below 9%, causes an increase of the t-ZrO₂ content. The critical value of the oxygen vacancy concentration for the tetragonal form is 3%. A further increase of the oxygen content to 1.07 X 10⁰ Pa and a decrease of oxygen vacancy concentration to 0.5% lead to the appearance of m-ZrO₂.

The C+T-ZrO₂ phase content is around 85% and 92% for vacuum and air, respectively. These behavior justify the higher densification in samples sintered in air, see Table 1. In this case, during the cooling, after sintering, a higher

martensitic (T-M transformation result in volumetric expansion of the bulf (3-5vol.%) and increase the crack formation, reducing the strength and fracture toughness of this ceramic [1, 17,18].

Then, samples sintered in vacuum, present lower content of cubic and tetragonal-ZrO_2 phases that samples sintered in air, reducing the toughening and consequently, the fracture strength of this ceramic. On the other hand, the proportion between tetragonal and cubic-ZrO_2 phases are similar and correspond to 65 and 35%, respectively, independently of the sintering atmosphere used.

Figure 5 shows micrograph of ceramic samples obtained by SEM.

It can be observed in Figure 5, grains with refined morphology in both sintering atmosphere conditions. These ceramics present grain size average near to 2μm without exaggerated grain growth, independently to the atmosphere. This refined microstructure can leads to the high fracture toughness improving the mechanical properties of these materials. Furthermore, no significant morphological differences are observed.
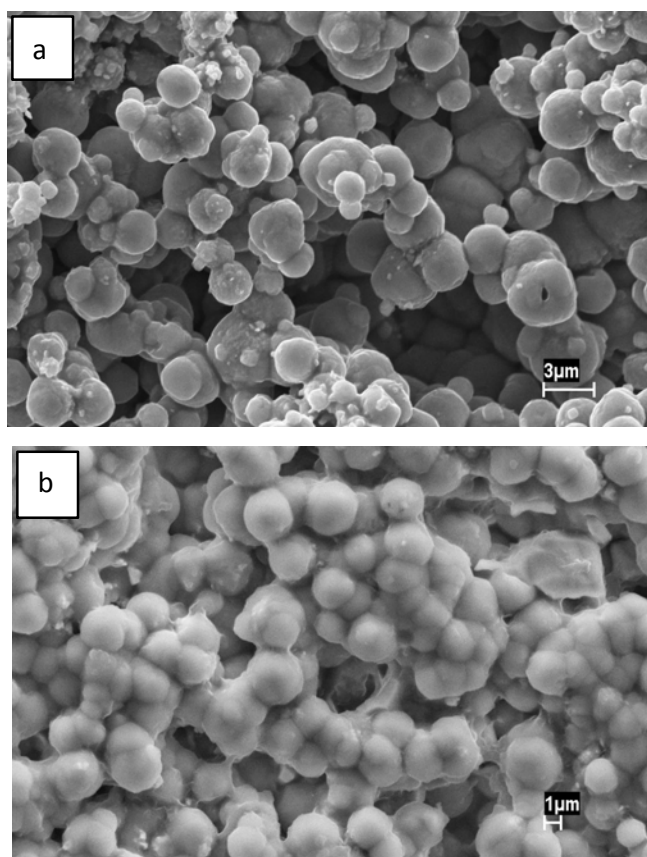

Figure 5 - Micrographs of ZrO_2-8wt.%Y_2O_3 samples sintered at 1600ºC obtained by SEM: a) in vacuum and b) in air.

4. CONCLUSIONS

Partially Stabilized Zirconia (PSZ) ceramic doped with 8%Y_2O_3 was obtained *in situ* at 1600ºC, using different sintering atmospheres (vacuum and air) by the ZrO_2-Y_2O_3 powder mixture. In both conditions, high Tetragonal+Cubic-ZrO_2 phase contents, near to 90%, were stabilized. Densification is higher to 88% of the theoretical density, and the refinement of the crystallographic parameters indicates similar lattice parameters of cubic and tetragonal phases independently to the sintering atmosphere. These similarity reflect to the microstructure which present refined grains morphology with grain size average near to 2μm, in both conditions (vacuum and air).

REFERENCES

1. STEVENS, R., *An Introduction to Zirconia: Zirconia and Zirconia Ceramics*, 2nd Ed Magnesium Elektrum, Munich, 1986.
2. CANOVA, I.C.; SOUZA, D.P.F.; COSTA, N.R.; SOUZA, M.F., *Mat. Res.* 2 (1999) 211.
3. VAN VALZAH, J.R.; EATON, H.E., *Surf. Coat. Technol. 46* (1991) 289.
4. BRATTON, R.J.; LAU, S.K., *Advances in Ceramics 3: Science and Tecnology of Zirconia,* American Ceramic Society, New York, 1981, p. 226.
5. SUBBARAO, E.C., *Advances in Ceramics 3: Science and Tecnology of Zirconia,* American Ceramic Society, New York, 1981, p. 1.
6. SCOTT, H.G., *J. Mat. Sci. 10* (1975) 1527.
7. HANNINK, R.H.J., KELLY, P.M., MUDDLE, B.C., *J. Am. Ceram. Soc. 83* (2000), 461.
8. RUH, R.; GARRET, H.J., J. Am. Ceram. Soc. 50 (1967) 257.
9. MILLER, R.A., *Advances in Ceramics 3: Science and Tecnology of Zirconia,* American Ceramic Society, New York, 1981, p. 241.
10. LEE, W.E.; RAMFORTH, W.M., *Ceramic Microstructures Property Control by Processing*, Chapman and Hall*,* London, 1994.
11. TOMASZEWSKI, H.; GODWOD, K., *J. European Ceramic Society 15* (1995 17.
12. ASTM-C744-74, *Standard Method for Density*, Pennsylvania, 1974.
13. PETZOW, G., Metallographie Etching, 2nd ed., ASTM International, Ohio, 1999.
14. OLIVEIRA, M.C.; CAIRO C.A.A., Proceedings of 21º Congresso Brasileiro de Cerâmica, Brasília, 1987, 533.
15. JCPDS – International Center for Diffraction Data. Swarthmore, 1979.
16. TOMASZEWSKI H.; GODWOD, K., *J. European Ceramic Society 15* (1995) 17.
17. NONO, M.C.A. *Cerâmicas de Zircônia Tetragonal Policristalina Estabilizada com Céria (Ce-TZP)*, Doctoral Thesis, ITA, São José dos Campos, 1990.
18. REIS, D.A.P.; ALMEIDA, D.S.; NONO, M.C.A.; SILVA, C.R.M.; PIORINO NETO, F., *Mat. Sci. Forum* 498-499 (2005), 546.