



Comparative Study of the Microstructural Properties of PSZ Zirconia Sintered in Vacuum and in Air

D.A.P. Reis¹; D.S. Almeida²; C.R.M. Silva³; M.C.A. Nono⁴; F. Piorino Neto⁵; M.J.R. Barboza⁶ e C. Santos⁷.

^{1,3} Instituto Tecnológico de Aeronáutica, ITA, SJCampos, Brazil.
danielireis@hotmail.com

^{2,5} Comando-Geral de Tecnologia Aeroespacial, IAE, SJCampos Brazil.

³ Universidade de Brasília, UNB, Brasília, Brazil.

⁴ Instituto Nacional de Pesquisas Espaciais, INPE, SJCampos, Brazil.

^{6,7} Escola de Engenharia de Lorena, EEL-USP, DEMAR, Lorena, Brazil.

ABSTRACT

Thermomechanical and electrical properties of zirconia-based ceramics have led to a wide range of advanced and engineering ceramic applications like solid electrolyte in oxygen 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 compared the properties of partially stabilized zirconia (PSZ) with 8 wt% of yttria sintered in vacuum and air at 1600°C. The microstructural investigation was done using Scanning Electron Microscope, X Ray Diffraction and density analysis. The values of samples density showed that the sintering in air was favorable to the material densification. The samples sintered in air showed dark color because the oxygen deficit. Besides this, the samples sintered in air presented higher conversion of the monoclinic phase to the tetragonal and cubic phases. The lattice parameters were calculated to the tetragonal and cubic phases and showed similar in both conditions (vacuum and air).

Key words: PSZ zirconia, sintering, densification.



INTRODUCTION

Zirconia has intrinsic physical and chemical properties, including hardness, wear resistance, low coefficient of friction, elastic modulus, chemical inertness, ionic conductivity, electrical properties, low thermal conductivity, and high melting temperature, that make it attractive as an engineering material and the focus of continued effort to understand and improve its mechanical behavior [1].

Pure zirconium oxide is an allotropic material and has three polymorphic phases that are stable in different temperature ranges. The cubic and tetragonal phases usually become stabilized at room temperatures by doping with ions such as rare earth, yttrium, calcium and magnesium. Doping introduces oxygen ion vacancies that can increase the ionic conduction by several orders of magnitude [2]. Zirconia has a cubic structure from its melting point at 2680°C down to 2370°C, where it transforms to a tetragonal structure. 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 [3]. 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 [3-6].

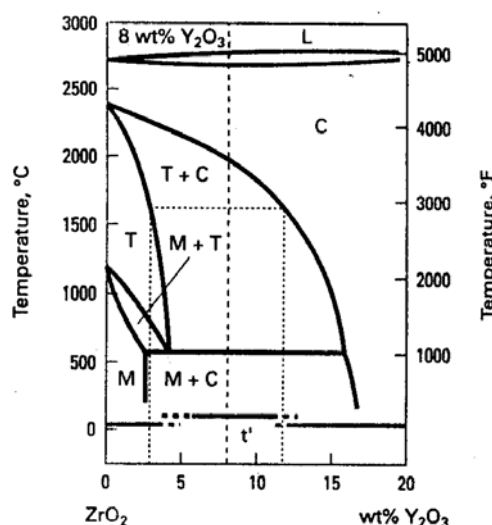


Figure 1 – Phase diagram of the ZrO₂-rich region of the ZrO₂-Y₂O₃ system [6].



Partially stabilized zirconia (PSZ) generally consisting of a cubic-ZrO₂ matrix with a dispersed tetragonal precipitates [7]. Specimens containing oxygen-deficient ZrO₂ have a very high affinity for oxygen [8]. Partially stabilized zirconia, with about 6.5 to 9 wt% Y₂O₃, 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 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 phase, t', which has a lower c/a ratio than the normal tetragonal and contains the same quantity of yttria as the cubic [10].

Transformation toughening in ZrO₂-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 ZrO₂ [11].

MATERIALS AND METHODS

The ZrO₂ powder used was produced and calcined (900°C for 2 h) by Instituto de Pesquisas Energéticas (IPEN) with 97,5% of purity. The Y₂O₃ powder used had 99,6% of purity by H.C. Starck. The mixture of 8%wt of Y₂O₃ 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 and in air. The sintering temperatures used were 1600°C during 30 min. The study of PSZ sintered was done using Scanning Electron Microscope (SEM), X Ray Diffraction



(XRD) and density analysis.

The $\text{ZrO}_2 + 8\text{wt}\% \text{Y}_2\text{O}_3$ samples were prepared using usual ceramography methods. To the grain boundary and porosity development used acid attack with phosphoric acid 85% at 250°C [12].

RESULTS AND DISCUSSION

The relative density was measured using a methodology based in Archimedes principle and considers the theoretical density [13]; it used the value of 6,05 g.cm⁻³ to the Y-PSZ [10].

The value of relative density for a green $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ sample was 50,13%. Table 1 shows the values of relative density to the $\text{ZrO}_2 + 8\text{wt}\% \text{Y}_2\text{O}_3$ samples sintering in vacuum and in air. The values of samples density showed that the sintering in air was favorable to the material densification. The samples sintered in air showed dark color because the oxygen deficit. Table 2 shows the values of linear shrinkage to the $\text{ZrO}_2 + 8\text{wt}\% \text{Y}_2\text{O}_3$ samples sintering in vacuum and in air.

Table 1 – Values of relative density obtained to the $\text{ZrO}_2 + 8\text{wt}\% \text{Y}_2\text{O}_3$ samples sintering in vacuum and in air.

| Sample | Relative Density (%) |
|--------|----------------------|
| vacuum | 88,81 |
| air | 93,73 |

Table 2 – Values of linear shrinkage obtained to the $\text{ZrO}_2 + 8\text{wt}\% \text{Y}_2\text{O}_3$ samples sintering in vacuum and in air.

| Sample | Linear Shrinkage (%) |
|--------|----------------------|
| vacuum | 17,59 |
| air | 16,67 |

Fig. 2 to 4 shows the X ray diffraction pattern of the ZrO_2 powder and of the $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ sintered samples in vacuum and in air, respectively. The identification of



phases present in ZrO_2 was done using JCPDS files [14] n^o 13-307 to monoclinic phase, 17-923 to tetragonal phase and 27-997 to cubic phase. In both cases (vacuum and air) observed the same phases converted.

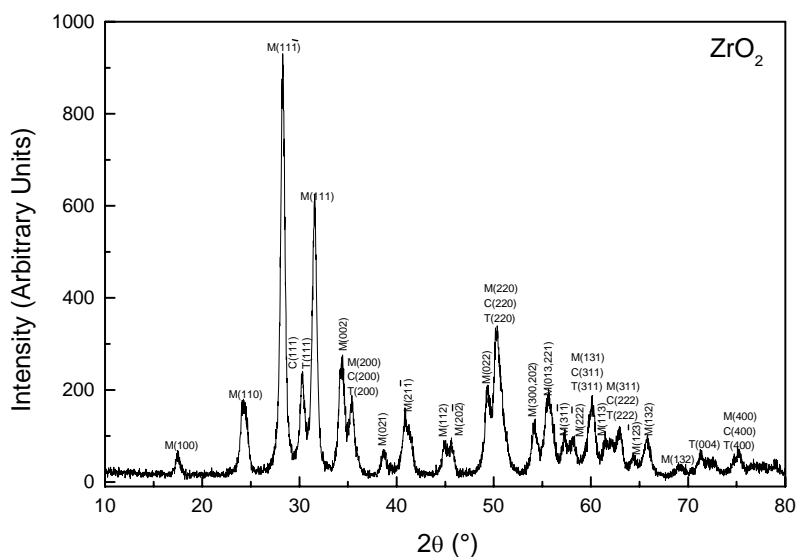


Figure 2 - X Ray Diffraction obtained for ZrO_2 powder.

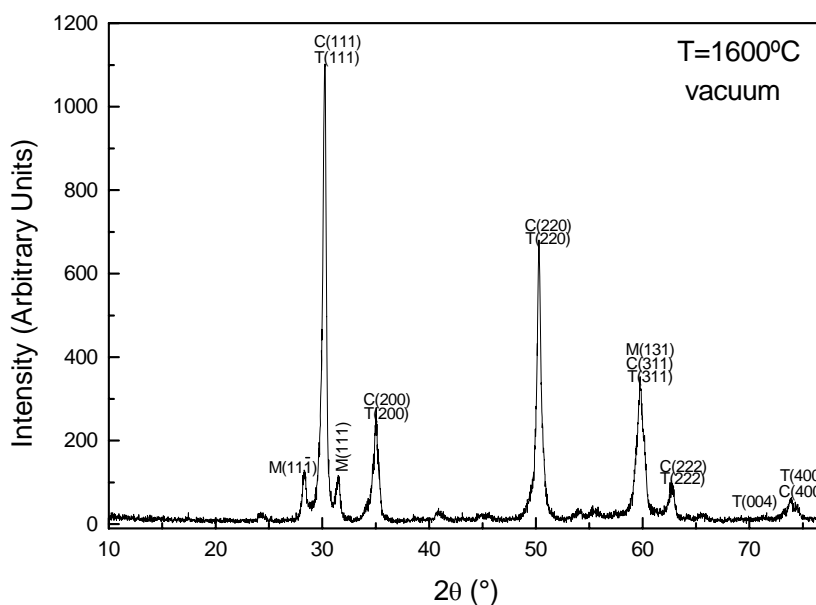


Figure 3 - X Ray Diffraction obtained for $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ sample sintered at 1600°C in vacuum.

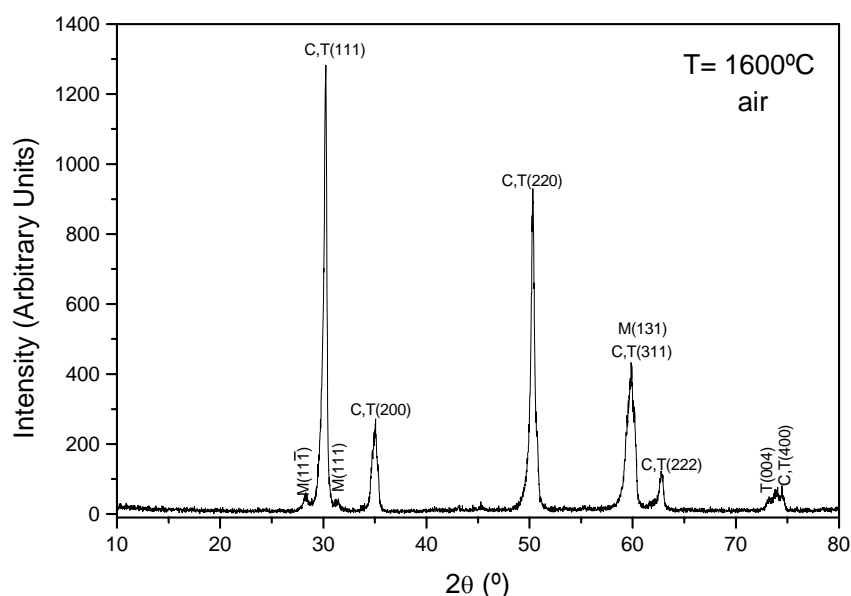


Figure 4 - X Ray Diffraction obtained for $ZrO_2 + Y_2O_3$ sample sintered at 1600°C in air.

The quantitative analysis of phases present in ZrO_2 based ceramics is so important to the study of tetragonal (t) – monoclinic (m) phase transformation and its relation with material hardening [15,16]. 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 [9]:

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

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

$$M + T + C' = 1.00 \quad \text{Eq.3}$$



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 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 3 shows the phase contents and lattice parameters of ceramic samples sintered at 1600°C in vacuum and in air. The lattice parameters were calculated and showed similar in vacuum and in air. The sample sintered in air presented higher conversion of the monoclinic phase to the tetragonal and cubic phases.

Table 3 – 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) |
| 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 |

Fig. 5 shows micrograph of ceramic samples obtained by SEM. The acid attack revealed the sample porosity. The air sintering was favorable to the densification through of the decreasing of the porosity.

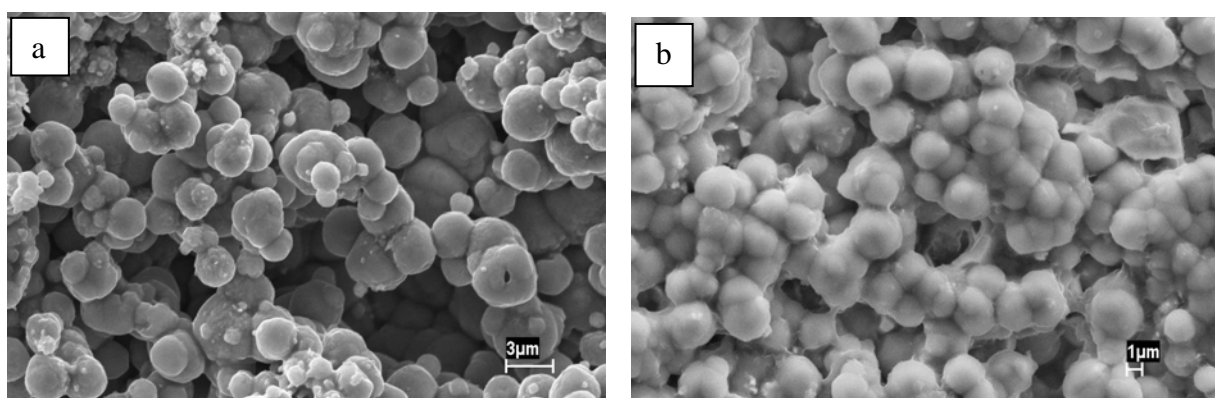


Figure 5 - Micrographies of ZrO_2 - Y_2O_3 samples sintered at 1600°C obtained by MEV: a) in vacuum and b) in air.



CONCLUSIONS

The values of samples density showed that the sintering in air was favorable to the material densification. The samples sintered in air showed dark color because the oxygen deficit. Besides this, the samples sintered in air presented higher conversion of the monoclinic phase to the tetragonal and cubic phases. The lattice parameters were calculated to the tetragonal and cubic phases and showed similar in both conditions (vacuum and air).

ACKNOWLEDGEMENTS

To FAPESP (Proc. 02/04736-7) for financial support, and to the Energetic Researches Institute (IPEN) for the ZrO₂ donation.

REFERENCES

- [1] S.P.S. Badwal, M.J. Bannister, R.H.J. Hannink (Eds.), Technomic, Lancaster, PA, 1993.
- [2] I.C. Canova, D.P.F. Souza, N.R. Costa, M.F. Souza, Materials Research 2 (1999), p. 211.
- [3] J.R. Van Valzah, H.E. Eaton, Surf. Coat. Technol. 46 (1991), p. 289.
- [4] R.J. Bratton, S.K. Lau, Adv. Ceram. 3: Science and Tecnology of Zirconia, American Ceramic Society (1981), p. 226.
- [5] E.C. Subbarao, Adv. Ceram. 3: Science and Tecnology of Zirconia, American Ceramic Society, pp. 1-13 (1981).
- [6] H.G. Scott, J. Mat. Sci. 10 pp.1527-1535 (1975).
- [7] R.H.J. Hannink, P.M. Kelly, B.C. Muddle, J.Am. Ceram. Soc. 83, pp.461-487 (2000).
- [8] R. Ruh, H.J. Garret, J. Am. Ceram. Soc. 50, pp.257-261 (1967).
- [9] R.A. Miller, et al. Adv. in Ceram. 3 Science and Tecnology of Zirconia, American Ceramic Society (1981) p.241.
- [10] W.E. Lee, W.M. Ramforth, Chapman and Hall, (1994) p.318.
- [11] H. Tomaszewski, K. Godwod, J. European Ceramic Society 15, pp.17-23 (1995).
- [12] G. Petzow, ASTM International, 2nd ed. (1999).



51º Congresso Brasileiro de Cerâmica

3 a 6 de junho de 2007 - Bahia Othon Palace Hotel - Salvador, BA

- [13] M.C. Oliveira, C.A.A. Cairo, et. al. Proceedings of 21º Congresso Brasileiro de Cerâmica, Brasília, pp.533-539 (1987).
- [14] JCPDS – International Center for Diffraction Data. Swarthmore, Pennsylvania (1979).
- [15] M.C.A. Nono, Doctoral Thesis, ITA, S. J. Campos (1990) p.50.
- [16] D.A.P. Reis et al. Materials Science Forum, 530-531, pp. 690-695 (2006).