MECHANICAL CHARACTERIZATION OF THE 3Y-TZP CO-DOPED WITH YTTRIA AND NIOBIA EQUIMOLAR ADDITION [1]

João Marcos kruszynski de Assis[2]
Daniele Ramos Dorat[3]
Flavia Baccaro Fonseca[4]
Francisco Cristóvão Lourenço de Melo [5]
Danieli Aparecida Reis [6]
Francisco Piorino Neto[5]
Maria do Carmo de Andrade Nono[7]

Abstract

The main goal of this work is to study the effect of the yttria and niobia equimolar addition in the 3Y-TZP on the mechanical properties (hardness, fracture toughness and four point bending strength) aiming to get a stable tetragonal phase (t´) under applied stress, to use as TBC´s. Four compositions with equimolar addition of yttria and niobia in the 3Y-TZP were produced, 13%, 14.5%, 16% and 17.5%. The mixtures were prepared in high energy ball milling for 10 minutes and the samples prepared on uniaxial and isostatic pressing. The selected temperature sintering was 1.550°C for 1 hour. Analyses of X-Ray Diffraction, hardness, fracture toughness and four point bending strength were performed. An increase on the mechanical properties analyzed was expected with yttria and niobia addition in comparision to 3Y-TZP, but instead a decrease was observed after these additions.

Key words: Mechanical characterization; Zirconia; Yttria; Niobia.

EFEITO DA TEMPERATURA DE SINTERIZAÇÃO NA 3Y-TZP CO-DOPADA COM ADIÇÃO EQUIMOLAR DE ÍTRIA E NIÓBIA

Resumo

Estudar o efeito da adição equimolar de ítria e nióbia sobre as propriedades mecânicas (microdureza, tenacidade à fratura, flexão de quatro pontos) da 3Y-TZP através da formação de fases tetragonais estáveis (t´) sob esforço mecânico, para aplicação em TBC. Foram preparadas quatro composições com adição equimolar de ítria e nióbia, 13%, 14,5%, 16% e 17,5% de $YO_{1,5}$ e $NbO_{2,5}$, numa zircônia tetragonal policristalina (3Y-TZP). Os pós foram moidos em moinho de alta energia por 10 minutos; as pastilhas foram prensadas uniaxial e isostaticamente, e sinterizados por 1 hora em 1.550°C. Foram realizadas análises de difração de raios X, microdureza Vickers, tenacidade à fratura por indentação, ensaios de flexão de quatro pontos e ensaio biaxial. Esperava-se um aumento das propriedades mecânicas analisadas em relação a 3Y-TZP sem adição de ítria e nióbia mas foi observado um decréscimo nestas propriedades com estas adições.

Palavras-chave: Caracterização mecânica; Zircônia; Ítria; Nióbia.

---

[1] *Contribuição técnica ao 65º Congresso Anual da ABM, 26 a 30 de julho de 2010, Rio de Janeiro, RJ, Brasil.*
[2] *Doutorando – Instituto Nacional de Pesquisas Espaciais- INPE e DCTA*
[3] *Aluna – PIBIC - Universidade do Vale do Paraíba - UNIVAP*
[4] *Aluna - PIBIC - Escola de Engenharia de Lorena – EEL - USP*
[5] *Doutor - Departamento de Ciência e Tecnologia Aeroespacial - DCTA*
[6] *Doutora – Instituto Tecnológico de Aeronáutica - ITA*
[7] *Doutora – Instituto Nacional de Pesquisas Espaciais - INPE*

1 INTRODUCTION

The martensitic transformation in zirconia was the first study of Garvie(1) made to improve mechanical strength of the ceramic materials, caused by its volumetric expansion of unitary crystalline cell and shearing tension in the t→m transformation, capable to enhance the fracture toughness, hardness and rupture tension.

An additional tetragonal phase in zirconia occurs under certain parameters like temperature, cooling and compositions,(2) and it's capable to improve fracture toughness with the increase of its tetragonality. This is namely **t´** and is formed by a displacive transformation from cubic phase, maintained the same compositions from the cubic zirconia.(3) The **t´** is called non-transformable metastable tetragonal phase with high yttria contents, stable under applied stress(4,5) and also called ferroelastics materials. This phase is well formed in a 3Y-TZP by sintering at longer times at 1.550°C.(2) To enhance the tetragonality, equimolar additions of trivalents and pentavalents oxides are used to increase the pentavalent oxide's solubility at the zirconia's net. The trivalent oxides are known as stabilizers and create oxygen vacancies in the net of zirconia. The pentavalents oxides are known as destabilizers and are used to annihilating oxygen vacancies, increasing the tetragonality.(6-8)

2 MATERIALS AND METHODS

The 3Y-TZP used was a nanostructured tetragonal zirconia polycrystalline stabilized with 3% mol of yttria of Shandong Zhongshun Sci. & Tech. Dev. Co. Ltd, with average size of particles between 20 and 30 nm. The niobia was produced by CBMM – Companhia Brasileira de Mineração e Metalurgia and the yttria was produced by H. C. Stark. Four compositions were produced, 13.0%, 14.5%, 16.0% and 17.5% of equimolar addition of $YO_{1.5}$ and $NbO_{2.5}$. The dry mixtures were prepared in high energy ball milling for 10 minutes. The samples were pressed in the uniaxial pressing accomplished with pressure of 100 MPa and the isostatic pressing with pressure of 300 MPa. The sintering temperature chosen was 1550°C for 1 hour. Analyses of conventional x-ray diffraction and measures of specific mass by Archimedes method were performed. The theoretical specific mass was calculated by the rule of mixtures. The mechanical characterization was performed by Vickers microhardness, fracture toughness through Vickers indentation and four point bending strength.

3 RESULTS

Table 1 shows the results of specific mass, porosity, and mechanical characterizations: Vickers microhardness, four point bending strengths and fracture toughness by Vickers indentation.

Table 1. Properties of samples sintered at 1550°C

samples	$\rho_{(Archimedes)}$ (g/cm^3)	ρ_R (%)	P (%)	H_v (GPa)	σ (MPa)	K_{1C} (MPa.m$^{1/2}$)
3Y-TZP	5.76	95.52	0.57	13.6 ± 0.5	219 ± 42	6.60 ± 0.77
13.0 %	5.32	93.49	0.23	9.7 ± 0.2	146 ± 13	2.45 ± 0.48
14.5 %	5.21	92.21	0.49	9.1 ± 0.5	114 ± 7	4.25 ± 1.05
16.0 %	5.12	91.27	0.55	9.0 ± 1.6	103 ± 13	4.98 ± 0.63
17.5 %	5.15	92.46	0.61	8.5 ± 0.8	110 ± 8	3.35 ± 0.63

ρ = Archimedes´s specific mass; ρ_R = relative specific mass; P =porosity; H_v = Vickers microhardness; σ = rupture stress; K_{1C} = fracture toughness.

The Figure 1 to 3 shows the linear regression of specific mass, Vickers microhardness and rupture tension in relation of yttria and niobia additions.

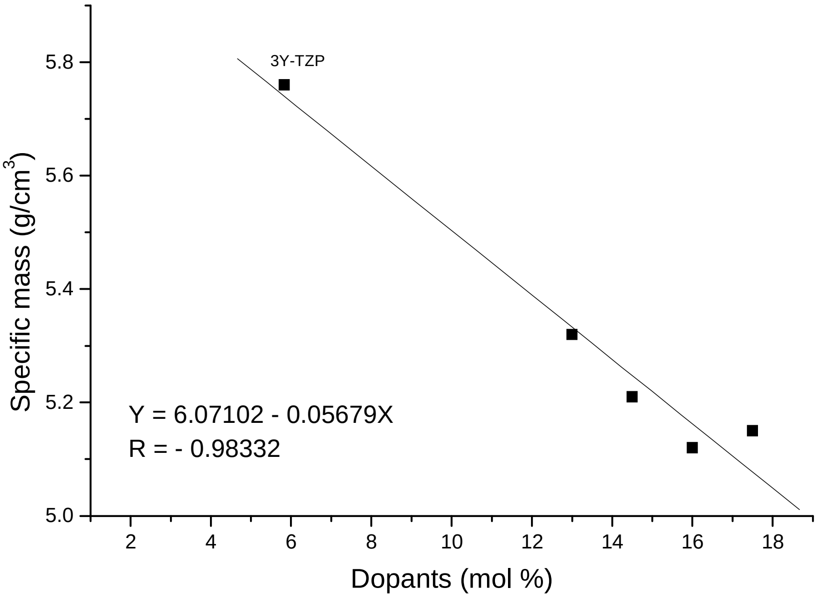

Figure 1- Linear regression of specific mass versus $YO_{1.5}$ and $NbO_{2.5}$ additions.

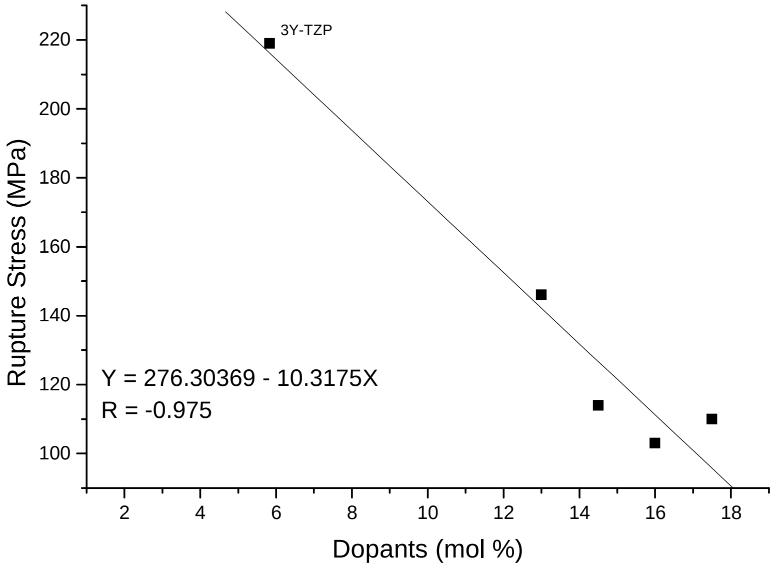

Figure 2- Linear regression of rupture stress versus $YO_{1.5}$ and $NbO_{2.5}$ additions.

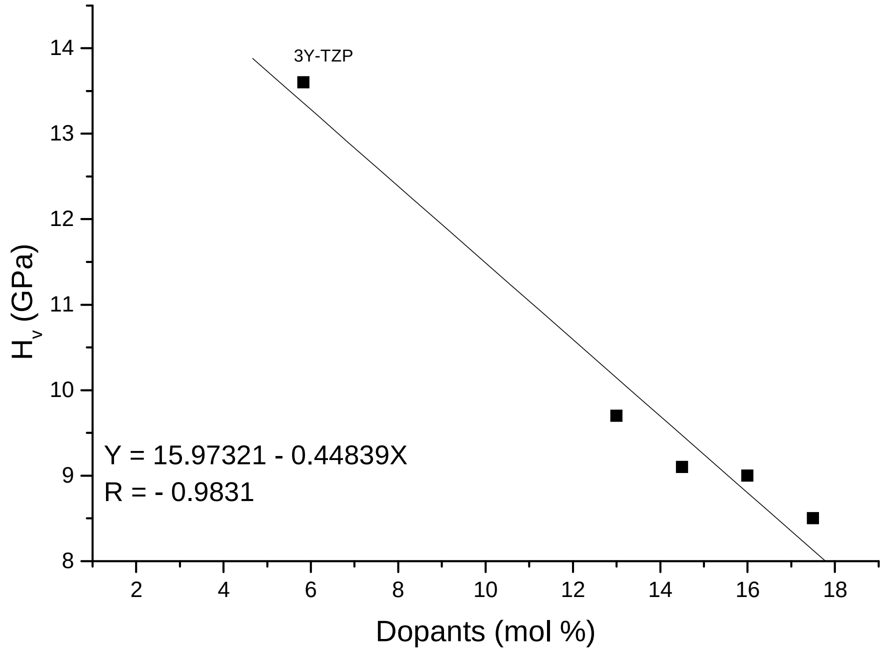

Figure 3- Linear regression of Vickers microhardness versus $YO_{1.5}$ and $NbO_{2.5}$ additions.

Figure 4 to 8 shows the x-ray diffractions of all samples sintered at 1550^{o}C.

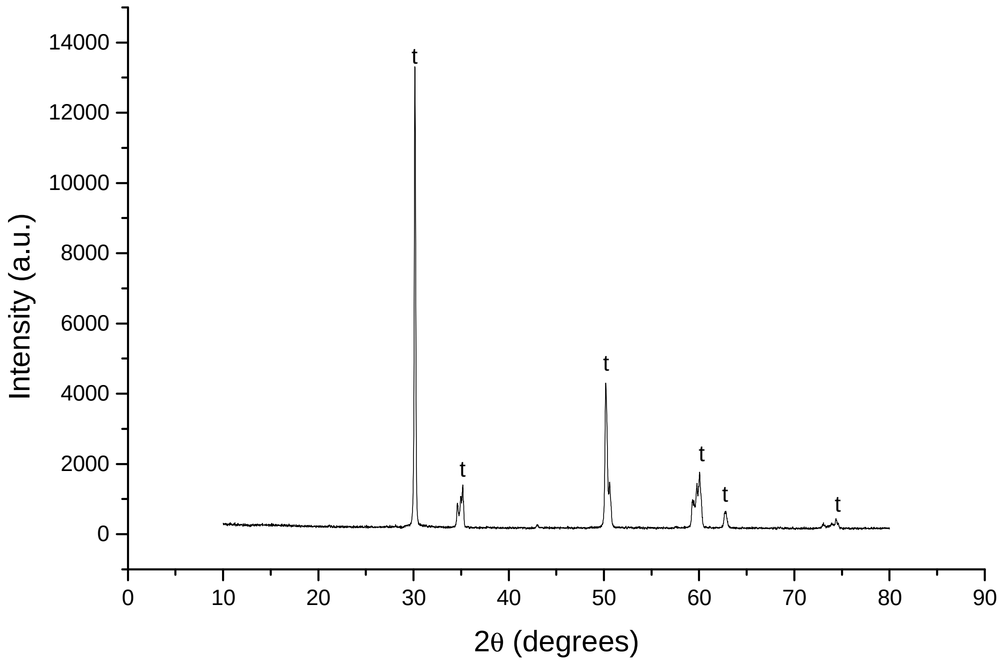

Figure 4- X-ray diffraction of 3Y-TZP sample sintered at 1550 ^{o}C.

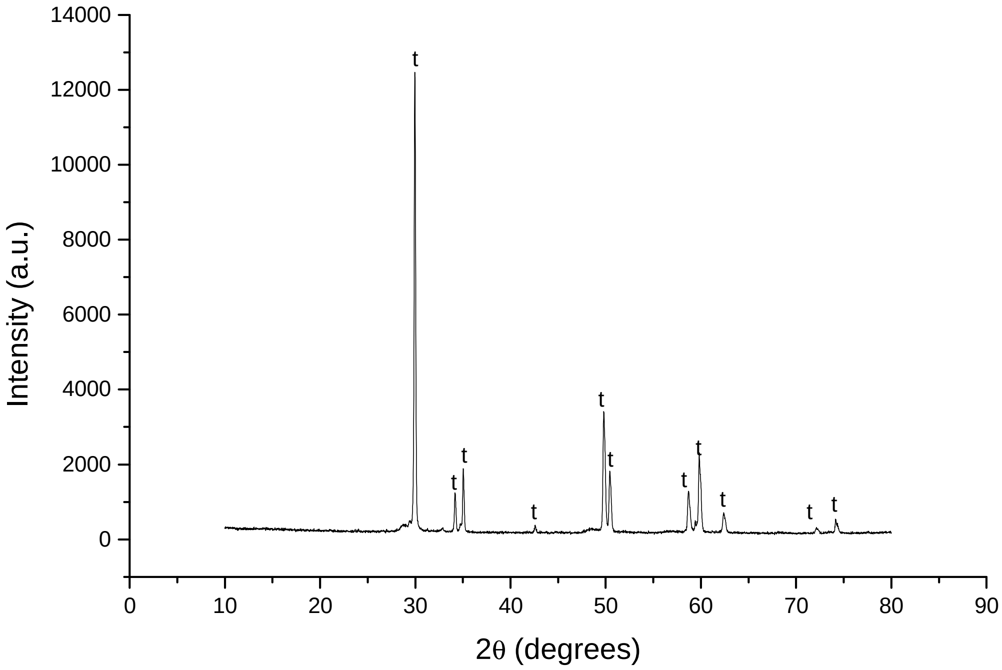

Figure 5- . X-ray diffraction of 13.0 % sample sintered at 1550 °C.

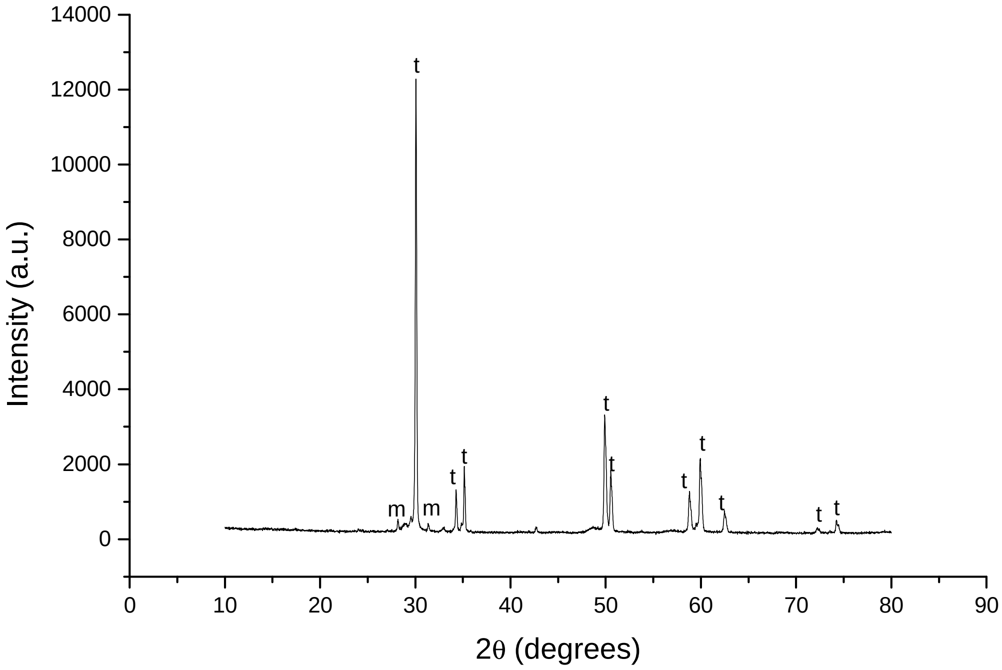

Figure 6- X-ray diffraction of 14.5 % sample sintered at 1550 °C.

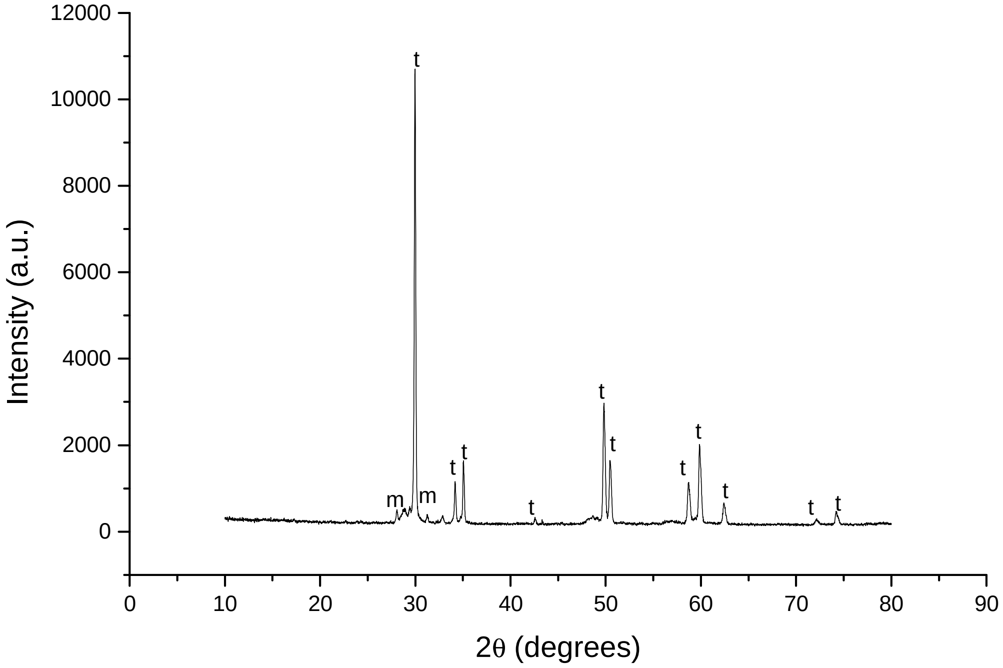

Figure 7- X-ray diffraction of 16.0 % sample sintered at 1550 ^{o}C.

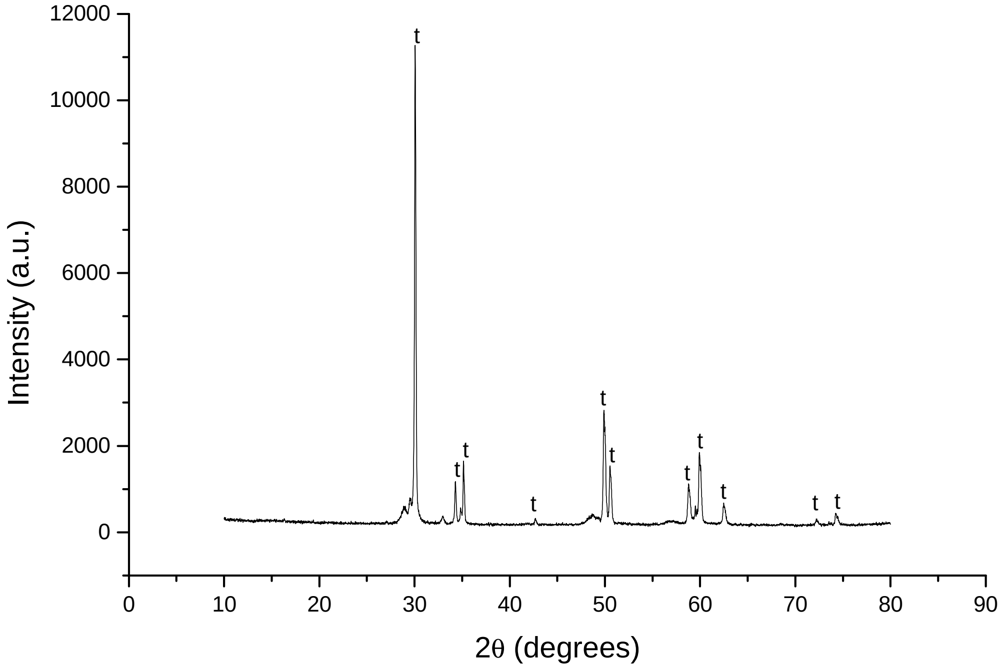

Figure 8- X-ray diffraction of 17.5 % sample sintered at 1550 ^{o}C.

4 DISCUSSION

The higher specific mass for 3Y-TZP reflects higher mechanical properties. Its x-ray diffraction revealed the single tetragonal phase without any trace of cubic phase. The literature(2) refers to the Y-TZP with 2-3 mol % Y_2O_3 contained a small amount of cubic phase, with grain usually larger than the tetragonal. When yttria and niobia were additioned to tetragonal zirconia, the relative specific mass decreased and this affected its mechanical properties. In the Figures 1 to 3, the linear regression shows a negative correlation coefficient, indicating a decreasing of specific mass,(9) Vickers microhardness and rupture stress, with the addition of niobia and yttria. However, the linearity doesn't occur to the fracture toughness data.

The x-ray diffraction in the Figures 5 and 8, that corresponds to samples with 13.0 % and 17.5 % of equimolar additions also shows single tetragonal phase, but samples with 14.5 and 16.0 % shows, in the Figure 6 and 7, two phases: tetragonal and monoclinic. This may help explaining the fracture toughness higher for these samples with monoclinic phase, caused by the martensitic transformation that may be occurred. The increases of tetragonality are responsible for the increase of fracture toughness. The trivalents oxides, creating oxygen vacancies and decreasing the tetragonality also decreasing the c/a ratio and approximating of cubic phases. On the other side Pentavalents oxides increases the tetragonality, approximating to monoclinic phases. Equimolar additions of trivalents and pentavalents oxides in zirconia are used to eliminate oxygen vacancies, increasing its tetragonality and approximating c/a ratio toward 1.020.(7,8,10) The addition of niobia in the 3Y-TZP was reported by other authors(11,12) to behavior as destabilizers of the tetragonal phase and decreases the amount of this phase in the samples.

Just as in inhomogeneous powders may occur the cubic phase in the Y-TZP(2), in this case, inhomogeneous powders obtained by dry milling could be responsible for the occurrence of monoclinic phase. These inhomogeneous powders could also be responsible for the worst results obtained to all properties measured with relation to the 3Y-TZP samples.

5 CONCLUSIONS

The equimolar addition of yttria and niobia to 3Y-TZP decreases the specific mass of samples because increases the tetragonality and c/a ratio approximating to a net parameters of monoclinic phase. However, its mechanical properties were affected by the inhomogeneous powders obtained by dry milling and this could result in a destabilization of 3Y-TZP due to different concentration of the co-dopant leading to the formation of a monoclinic phases and insufficient increases of its tetragonality to promote any improvement of fracture toughness and other mechanical properties. As the measured relative specific mass, was bellow 95% to all additions of co-dopant, It is possible that the sintering process could be affected by this in homogeneity causing the poor result obtained in all properties measured.

Acknowledgments

To Departamento de Ciência e Tecnologia Aeroespacial (DCTA), Instituto de Aeronáutica e Espaço (IAE), CNPq – CIAM project – process 4908451/2006-1, CNPq - PIBIC.

REFERENCES

1 GARVIE, R. C.; HANNINK, R. H.; PASCOE, R. T. Ceramic Steel. **Nature**, v. 258, n. 5537, p. 703-704, 1975.

2 LEE, W. E.; RAINFORTH, W. M. **Ceramic microstructures property control by processing**. Londres, Reino Unido: Chapman and Hall, 1994.

3 Heuer, A. H.; Chaim, R.; Lanteri, V. The displacive cubic-tetragonal transformation in ZrO_2 alloys. **Acta Metall.**, 35, p. 661-666, 1987.

4 YOSHIMURA, M. Phase Stability of Zirconia. **Ceramic Bulletin**, v. 67, n. 12, 1988.

5 HEUER, A. H., HOBBS, L. W., **Science and technology of zirconia**, Columbus, Ohio: The American Ceramic Society, 1981, p. 241.

6 LI, P.; CHEN, I.W.; PENNER-HAHN, J.E. Effect of Dopants on Zirconia Stabilization-An X-ray Absorption Study: III, Charge-Compensating Dopants. **J. Amer. Ceram. Soc.** n. 77 (5), (1994), p.1289-1295.

7 Kim, D. J.; Tien, T. Y. Phase stability and physical properties of cubic and tetragonal ZrO_2 in the system $ZrO_2 – Y_2O_3 – Ta_2O_5$. **Journal of the American Society**, v.12 , n. 74, p. 3061-65, 1991.

8 Lee, D. Y.; Kim, D. J.; Cho, D. H. Low thermal phase stability and mechanical properties of Y_2O_3 and Nb_2O_5 co-doped tetragonal zirconia polycrystal ceramics. **Journal of Materials Science Letters**, v. 17, p. 185-187, 1998.

9 ALMEIDA, D. S. **Estudo de revestimentos cerâmicos sobre substrato metálico, obtidos por deposição físico de vapores por feixe de elétrons para aplicação como barreira térmica**. 2005. 175f. Tese de Doutorado. Instituto Nacional de Pesquisas Espaciais - INPE, Brasil, 2005.

10 Kim, D. J. Effect of Ta_2O_5, Nb_2O_5, and HfO_2 alloying on the transformability of Y2O3-stabilized tetragonal ZrO2. **Journal of the American Ceramic Society**, v. 1, n. 73, p. 115-20, 1990.

11 YANG, S. et al. Sintering behavior of Y-doped ZrO_2 ceramics: the effect of Al_2O_3 and Nb_2O_5 addition. **Solid State Ionic,** v. 172, n. 1-4, p. 413-416, 2004.

12 JIN, X. H. et al. Effects of Nb_2O_5 on the stability of t-ZrO_2 and the mechanical properties of ZTM. **Materials Letters**, v. 52, n. 1-2, p. 10-13, 2002.