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THE EFFECT OF SINTERING TEMPERATURE ON THE 3Y-TZP CO-DOPED WITH EQUIMOLAR ADDITION OF THE YTTRIA AND NIOBIA[1]

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Abstract
The aim of this work is to identify the better sintering temperature to densify zirconia co-doped with yttria and niobia and to verify the existence of the stable tetragonal phase (t´) under applied stress at room temperature to be applied as a TBC material. Four compositions with equimolar addition of yttria and niobia in the 3Y-TZP were produced, 13.0 %, 14.5 %, 16.0 % 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 sintering temperatures were 1500°C, 1550°C, 1600°C and 1650°C, for 1 hour. Analysis of conventional and high resolution X-Ray Diffraction and measures of specific mass by Archimedes method were performed. Through measures of the specific mass, the best sintering temperature was 1550°C, with relative specific mass above 95 %. The x-ray diffraction analysis indicate a probable existence of t´ in all samples.
Key words: Zirconia; Yttria; Niobia.

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

Resumo
Estudo da temperatura de sinterização ideal para a densificação de cerâmicas de zircônia co-dopadas com ítria e nióbia, e da existência de fases tetragonais estáveis (t´) sob aplicação de tensões na temperatura ambiente, 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 quatro temperaturas diferentes: 1.500°C, 1.550°C, 1.600°C e 1.650°C. Foram realizadas medidas de massa específica pelo método de Arquimedes e análises de difração de raios X convencional e de alta resolução em ângulo rasante. Pelas medidas de massa específica concluiu-se que a melhor temperatura para a sinterização destas composições foi em 1.550°C, com massa específica relativa acima de 95 %. As análises de difração de raios X apontam para uma possível existência da fase tetragonal t´ em todas as composições estudadas.
Palavras-chave: Zircônia; Ítria; Nióbia.

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1 INTRODUCTION

Zirconia-based ceramics are indicated to be applied as structural materials because of their stress-assisted tetragonal-to-monoclinic transformation that's increase the mechanical properties.[1-4] This metastable tetragonal phase obtained during sintering in high temperatures[5,6] is retained at room temperature by the use of stabilizers. Additions of some oxides to pure zirconia depress allotropic transformations (crystal structure changes) and allow to stabilize either cubic or tetragonal structure of the material at any temperature. Yttria-stabilized zirconia is used as a TBC materials because its low thermal conductivity and a good chemical stability at elevated temperatures.[7] Trivalents and tetravalents stabilizers, like yttria, ceria and titania are used to obtain tetragonal phase in zirconia. Charge compensating dopants are also used, like $YNbO_4$ and $YTaO_4$,[6,8] that are obtained for equimolar addition to Y_2O_3 and Nb_2O_5 and Y_2O_3 and Ta_2O_5 respectively and develops a quasi-binary system.[9]
The equimolar addition with trivalent and pentavalent oxides are used to annihilating oxygen vacancies created at trivalents dopants additions for charge balance, and to increase the pentavalent oxide's solubility on the zirconia's net.[7,10,11] The niobia addition reduce the concentration and the mobility of oxygen vacancies, increasing the resistivity and affecting the original defect structure.[12,13]
Additions of yttria can stabilize the tetragonal phase with lower c/a ratio than the normal tetragonal phase.[8,14] This is called non-transformable metastable tetragonal phase with high yttria contents (t´), stable under applied stress[8,9] and so called ferroelastics materials, that also can be obtained with additions of trivalents and pentavalents oxides.

2 MATERIALS AND METHODS

The 3Y-TZP utilized 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 in pastille´s form with 10 x 10 mm 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. Four sintering temperatures were chosen, 1500°C, 1550°C, 1600°C and 1650°C for 1 hour. Analysis of conventional and high resolution x-ray diffraction and measures of specific mass by Archimedes method were performed. The theoretical specific mass was calculated by the rule of mixture. Determination of the t´ phase was performed with the high resolution x-ray diffraction analysis with low angle, in high 2θ (between 70° and 80°), before and after to grind surfaces of samples.

3 RESULTS

The table 1 shows the theoretical specific mass (calculated), specific mass measured by Archimedes methods, relative specific mass and porosity of all samples sintered in 1500°C, 1550°C, 1600°C and 1650°C.

Table 1. Properties of samples sintered in 1500°C, 1550°C, 1600°C and 1650°C

Samples	$\rho_{calculated}$ (g/cm^3)	$\rho_{Archimedes}$ (g/cm^3)	$\rho_{relative}$ %	Pa %
1500°C				
13.0 %	5.69	5.46	95.96	0.18
14,5 %	5.65	5.41	95.75	0.43
16.0 %	5.61	5.35	95.36	0.31
17.5 %	5.57	5.28	94.79	0.93
1550°C				
13.0 %	5.69	5.49	96.48	0.32
14,5 %	5.65	5.46	96.64	0.33
16.0 %	5.61	5.44	96.96	0.34
17.5 %	5.57	5.43	97.49	0.40
1600°C				
13.0 %	5.69	5.35	94.02	0.61
14,5 %	5.65	5.32	94.15	0.64
16.0 %	5.61	5.41	96.43	0.29
17.5 %	5.57	5.42	97.31	0.49
1650°C				
13.0 %	5.69	5.23	91.91	4.11
14,5 %	5.65	5.13	90.80	3.75
16.0 %	5.61	5.16	91.97	4.62
17.5 %	5.57	5.27	94.61	0.59

Pa = porosity

Figure 1 to 4 shows the conventional XRD patterns of samples sintered at 1500°C, 1550°C, , 1600°C and 1650°C. Figure 5 shows the conventional XRD patterns of samples sintered at 1550°C with 2θ between 70 and 80 degrees, and figure 6 shows high resolution XRD with low angle of samples sintered at 1550°C with 2θ between 70 and 78 degrees.

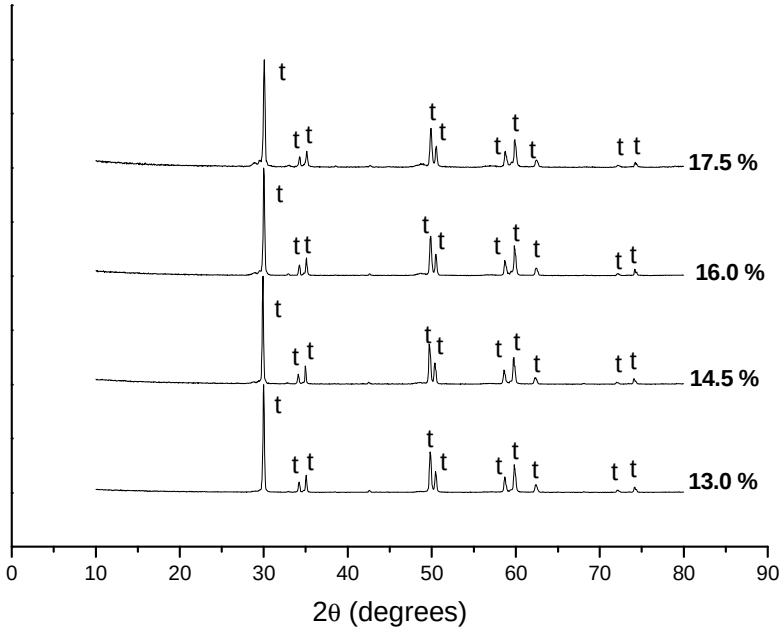

Figure 1. X-ray diffraction of samples sintered at 1500 °C

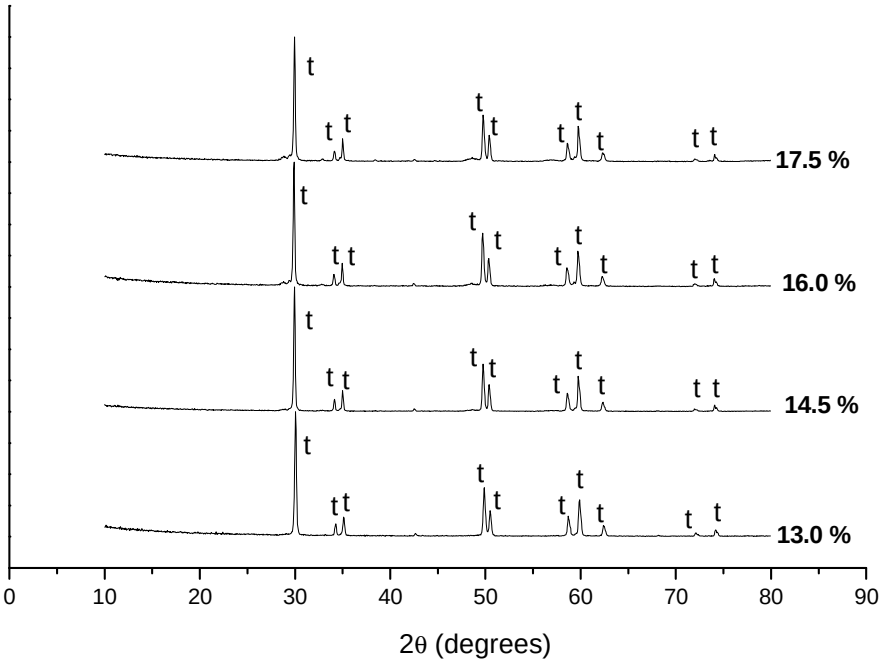

Figure 2. X-ray diffraction of samples sintered at 1550 °C

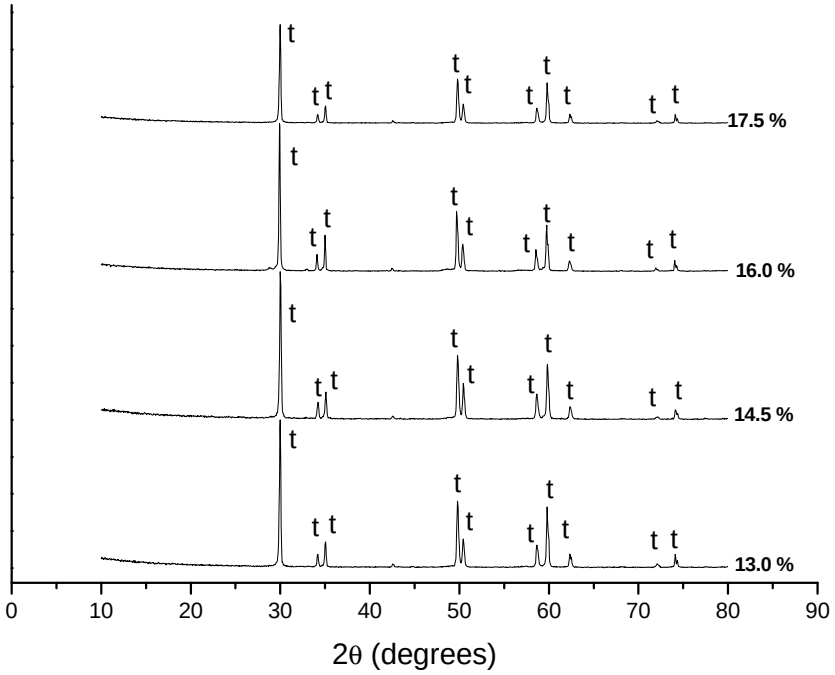

Figure 3. X-ray diffraction of samples sintered at 1600 °C

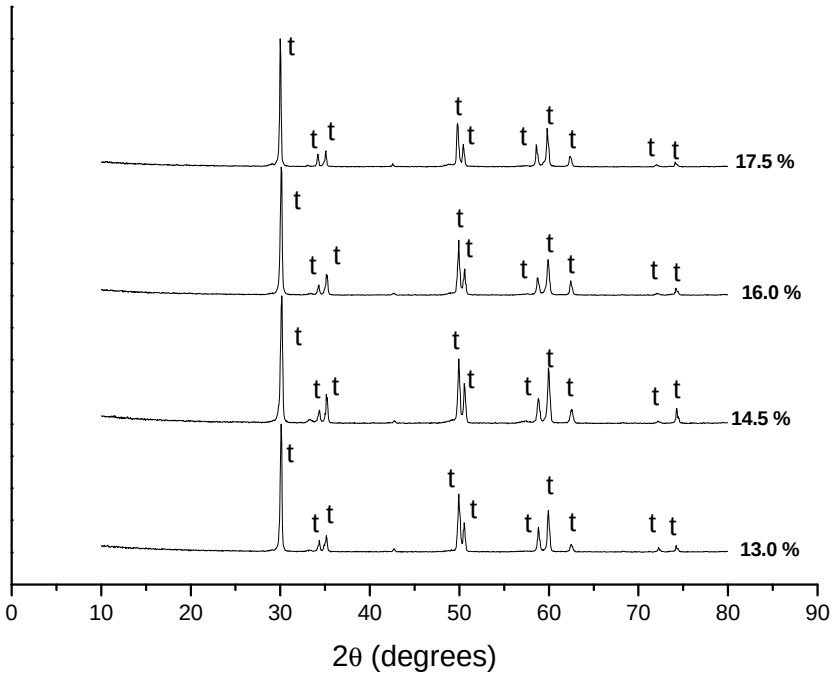

Figure 4. X-ray diffraction of samples sintered at 1650 °C

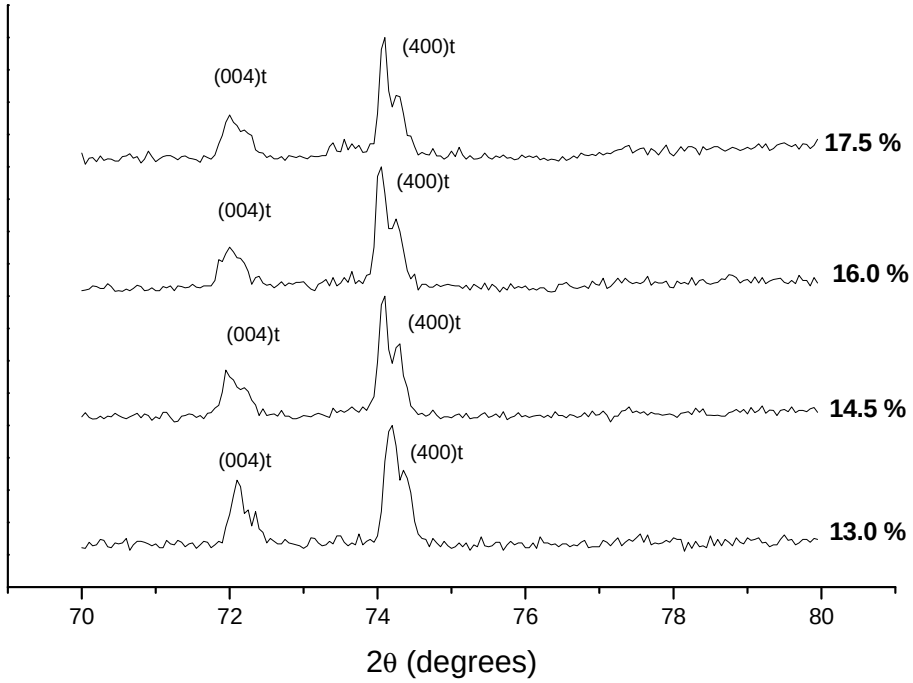

Figure 5. Conventional x-ray diffraction of samples sintered in 1550 °C

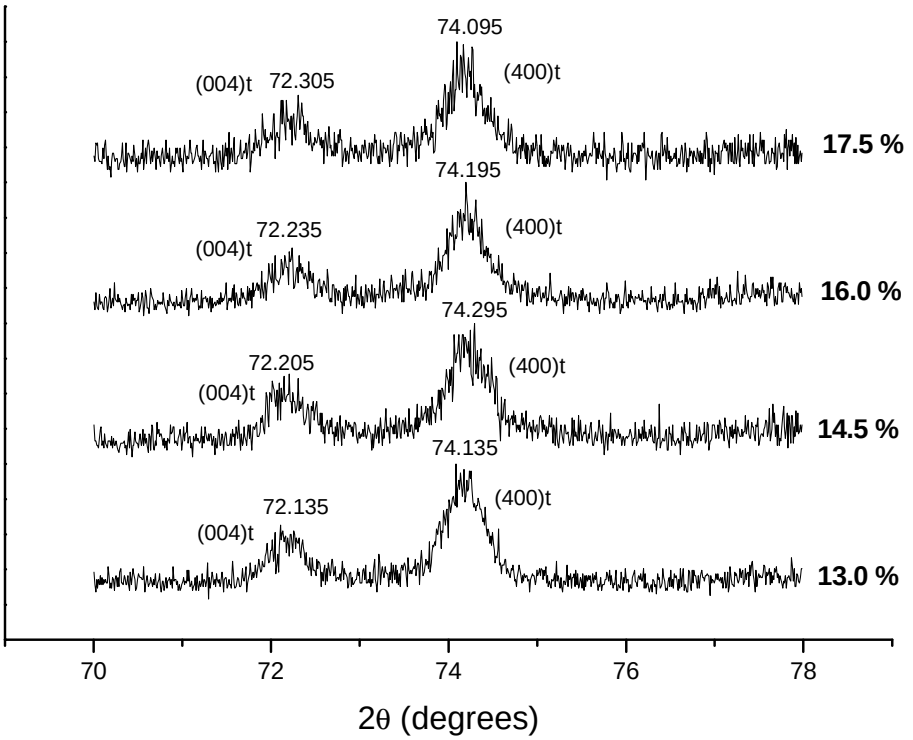

Figure 6. High resolution x-ray diffraction of samples sintered in 1550 °C.

4 DISCUSSION

When the rule of mixtures is used to calculate theoretical specific mass of sintered zirconia´s samples, the calculated density decrease as the yttria and niobia contents increase. This method doesn't take in account the diffusionless of Y^{3+} and Nb^{5+} in the net of zirconia to replace the Zr^{4+}, eliminating oxygen vacancies and increasing the tetragonality causing an increase on c/a ratio. Yttria stabilized zirconia in the tetragonal phase has theoretical specific mass at about 6.1 g/cm^3.(14)
Table 1 shows a decreasing of the real specific mass measured by Archimedes method at 1500^{o}C and 1550^{o}C following the same behavior of the specific mass calculated by the rule of mixtures. To the others sintering temperature the behavior shows to have no pattern but the specific mass increases for the 17.5 % content . At 1550^{o}C the specific mass is higher and porosity is lower than the others compositions. It could also be observed that the specific mass increase as the temperature increases up to 1550^{o}C, when it starts to decrease as the sintering temperature continues to increase.
The x-ray diffraction was used to determine the phases. All samples showed a tetragonal phase without a presence of a monoclinic or cubic phase. It is compatible to zirconia stabilized with equimolar addition(15) of a trivalent stabilizants as yttria and pentavalent dopants as niobia or tantala, because it eliminates oxygen vacancies. This phase is also found in coatings for TBCs obtained from these targets(15,16).
The conventional XRD patterns from Figure 5 shows the presence of tetragonal phase before grinding surfaces of samples as observed by others works.(15-17) The high resolution XRD patterns with low angle in Digure 6, after grinding surfaces of samples show that the tetragonal phase doesn't destabilize under applied stress, and it wasn't transformed to a monoclinic phase, indicating the probable existence of t´.

5 CONCLUSIONS

The best results of specific mass occured at 1550^{o}C. All relative specific mass in this temperature is over 96 % of the theoretical one. Others methods to calculate the theoretical specific mass should be applied in this case to consider net parameters, stabilizants contents and the peaks of XRD to obtain more trustful results. The x-ray diffraction shows the existence of a tetragonal phase in all samples, compatible with equimolar addition of trivalents and pentavalents stabilizants and the probable existence of a metastable non-transformable phase t´ under applied stress on surface of samples.

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