Study of ZrO₂ tetragonal phase stabilization as function of the yttrium and rare earth oxides mixture content

Carlos Kuranaga¹, Maria do Carmo de Andrade Nono¹

¹Instituo Nacional de Pesquisas Espaciais - INPE, Laboratório Associados de Sensores e Materiais - LAS Caixa Postal 515 - 12201-970 - São José dos Campos/SP
E-mail: Kuranaga@las.inpe.br and maria@las.inpe.br

Key words: tetragonal zirconia, phase stabilization, powder characterization

Abstract

In this work were reported and discussed the results for the crystalline tetragonal phase formation and stabilization of the zirconia as function of the temperature and yttrium and rare earth oxides mixture (YRE) content. The raw materials are of Brazilian origin. The powder mixtures were obtained from the yttrium and rare earth hydroxides and hydrous zirconia coprecipitation and calcined at 1400°C. The crystalline phase evolution of these powders as function of the YRE content was studied by X-ray diffraction. The lattice parameter refinements for the tetragonal and cubic phases were made using a computational program - TRIESTE. The parameter relationship c/a for the tetragonal unitary cell was determined and the results showed the tendency for the tetragonal phase stabilization. The values of the experimental lattice parameters for the tetragonal phase were compared with the calculated theoretical values using the mathematical model of vacancies. The two techniques used for the determinations of the lattice parameters presented excellent reliable results. The ZrO₂ tetragonal phase could be stabilized with 6 mol % of YRE.

Introduction

The pure zirconia possesses three crystalline forms: monoclinic, tetragonal and cubic [1], whose transformations follow the following sequence:

Monoclinic $\xrightarrow{1170 \degree C}$ Tetragonal $\xrightarrow{2370 \degree C}$ Cubic $\xrightarrow{2680 \degree C}$ Liquid

The addition of stabilization oxides is necessary to keep the polimorphic phases of high temperatures to room temperature [1,2,3].
The transformation tetragonal/monoclinic possesses enormous technological interest due to his martensitic nature, accompanied by an volumetric expansion from 3% to 5%. This provokes in the material external tensions that improve the mechanical properties. Therefore the presence of the phase tetragonal is a prerequisite for the hardening of the material, besides, this can delay and even interrupting the propagation of a trine. This happens due to transformation of the phase tetragonal in monoclinic through compress tensions [1,2,3].

Two exist broken for zirconia production starting from the zirconia: chemical processing and thermal processing [2,3].
The technological route adopted in this work is based on the chemical decomposition of the zirconia through an alkaline material that later is converted in chloride that is crystallized and purified [2,4]. After this stage this material can be calcined and if to obtain the zirconia or it can be doped and if to obtain partially stabilized zirconia (PSZ), tetragonal zirconia polycrystals (TZP) or cubic, depending on the concentration of the stabilization material added [2,3,4].
The knowledge of the present phase, monoclinic/tetragonal/cubic, is very important depending on the type of application of the material, be as structural ceramic (PSZ and TZP) or nobler applications as electrolyte solid, sensors, etc (cubic zirconia) [1,3].

The ceramic of tetragonal zirconia polycrystals (TZP) they are those that present phase stable tetragonal in the room temperature, as the tetragonal zirconia polycrystals stabilized with yttrium oxide (Y-TZP) [3], cerium oxide (Ce-TZP) [5] and other rare earths. In this material class the resistance to the flexing can reach values from 500 to 1300 MPa and tenacity to the fracture from 10 to 23 MPa.m$^{-1/2}$, depending on the stabilization material. Therefore, these ceramic present great potential as structural ceramic [5].

The ceramic of tetragonal zirconia polycrystals stabilized with yttrium and of rare earth oxides mixture (YRE) they are considered as alternative, due to her low processing cost [4,6].

In this work he took place a study of the influence of the yttrium and of rare earth oxides mixture (YRE) content in the stabilization of the zirconia, with the objective of obtaining the tetragonal zirconia polycrystals.

Experimental Procedure

The materials used in the preparation of the samples were: zircon, supplied by Paranapanema, and they were doped with yttrium and of rare earth oxides mixture (YRE) obtained starting from the xenotime, supplied by Paranapanema.

The samples were prepared for chemical decomposition of the zirconita, using NaOH, later HCl is added to obtain ZrOCl$_2$.8H$_2$O that is purified by crystallization [2,4].

After the crystallization stage, obtained ZrOCl$_2$.8H$_2$O was submitted to a chemical analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for determination of the purity.

The yttrium and of rare earth oxides mixture (YRE) also the chemical analysis was submitted by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for determination of the concentration of the yttrium and of the other rare earths.

After hydroxilation the mixtures of ZrO$_2$.xH$_2$O with different concentrations of hydroxide of yttrium concentrate and rare earths (0% to 5%, 5.5%, 6%, 7% and 10%) they were submitted the chemical analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) for confirmation of the concentrations of the added dopantes.

The samples were calcined to 1400°C and they were characterized by diffraction of ray-X with radiation Cuka.

For structural ceramic it is very used a mixture of the phases monoclinic and tetragonal (PSZ) or a zirconia totally tetragonal (TZP). For that we can know the proportions of the phase monoclinic and tetragonal an equation is used [1] proposed by Kosmac et al [7], the Eq. 1 is the following:

\[
X_m = \frac{I_m(111) + I_m(11 \bar{1})}{I_m(111) + I_m(11 \bar{1}) + I_s(111)}
\]

This formula bases on the results of diffraction of ray-X, where they are identified the (hkl) of the two present phases. In these calculations the picks of Bragg reflection are used (111) and (11-1) for the phase monoclinic and the (111) for phase tetragonal.

Results and Discussion

The chemical analysis of ZrOCl$_2$.8H$_2$O showed the presence of 36 ppm of Si, 20 ppm of Fe, 18 ppm of Ca, 12,4 ppm of Al, 7,6 ppm of Ti, 2,6 ppm of Mg and 2 ppm of Na. What proves that
the material presents low tenors of impurity, therefore it is an appropriate material for his use in the ceramic.

The cátions Ca and Mg are not considered as impurity, because these elements favor the stabilization of the zirconia [3].

The chemical analysis of the yttrium and of rare earth oxides mixture (YRE) presented the following concentrations: Y₂O₃ (44,35%); Yb₂O₃ (19,98%); Er₂O₃ (13,80%); Dy₂O₃ (10,17%); Ho₂O₃ (3,06%); Tm₂O₃ (2,76%); Lu₂O₃ (2,70%); Gd₂O₃ (1,18%); Tb₂O₇ (0,773%); Sm₂O₃ (0,388%); Nd₂O₃ (0,174%); Ce₂O₃ (0,166%); ThO₂ (0,045%); Eu₂O₃ (0,016%). This chemical analysis showed that the yttrium and of rare earth oxides mixture (YRE) contain stabilization elements of the zirconia, as it is the case of Y, Yb, Er, Dy, Ho, Tm, Gd, Tb, Sm, Nd, Ce and Me [8,9,10,11].

The chemical analysis of ZrO₂.xH₂O doped with different concentrations of hydroxide of yttrium and of rare earth mixture confirmed the presence of the dopantes in the proportions from 0% to 5%, 5,5%, 6%, 7% and 10%.

![Fig. 1: Diffraction of ray-X of the zirconia: a) without dopagem; b) 1%, c) 2%, d) 3%, e) 4%, f) 5%, g) 5,5% and h) 6% of yttrium and rare earth oxide mixture:](image)

The Fig. 1 display the diffractions of ray-X for the different concentrations of yttrium and rare earth oxide mixture (0% to 6%). Where we can notice that in the proportions from 0% to 2% of yttrium and of rare earth oxides mixture the phase is monoclinic (curves a); b) and c) of the Fig. 1). In these proportions the lattice parameters we re made calculations and these are shown in the Table I. can verify that the theoretical values and made calculations are close, proving that the present phase is monoclinic.

**Table I: Lattice parameters of the phase monoclinic.**

<table>
<thead>
<tr>
<th></th>
<th>Teórico</th>
<th>0%</th>
<th>1%</th>
<th>2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5,1477</td>
<td>5,1435</td>
<td>5,1480</td>
<td>5,1473</td>
</tr>
<tr>
<td>b</td>
<td>5,2030</td>
<td>5,192</td>
<td>5,209</td>
<td>5,225</td>
</tr>
<tr>
<td>c</td>
<td>5,3156</td>
<td>5,312</td>
<td>5,3083</td>
<td>5,2990</td>
</tr>
<tr>
<td>β</td>
<td>99°23'</td>
<td>99°21'</td>
<td>99°03'</td>
<td>99°03'</td>
</tr>
</tbody>
</table>

For the samples containing concentrations from 3% to 5,5% (curves d); e); f) and g) of the Fig. 1), there are a mixture of the phase monoclinic and tetragonal. What hinders the calculations of the lattice parameters.
Being used of the formula proposed by Kosmac et al. [7], it was calculated the percentile relationship of the phases monoclinics and present tetragonal in the samples containing 3%, 4%, 5% and 5.5%. Doping with 2% of yttrium and of rare earth oxides mixture presented 100% of the phase monoclinic (curves c) of the Fig. 1 and with 6% of yttrium and of rare earth oxides mixture are observed 100% of phase tetragonal (curves h) of the Fig. 1. These results are shown in the Fig. 2.

![Percentile relationship of phase versus concentration of YRE.](image1)

Fig. 2: Percentile relationship of phase versus concentration of YRE.

In her we can observe the decrease of the phase monoclinic (●) and the increase of the phase tetragonal (■). It is possible to verify that he enters the concentrations of 4% up to 5% of yttrium and of rare earth oxides mixture have an accentuated fall of the proportions of the phase monoclinic and an accentuated increase of the phase tetragonal.

In this work it was verified that these phases are present to room temperature, not being necessary the application of a quenching to stabilize the phase tetragonal.

![Diffraction of ray-X for the zirconias doped with yttrium and of rare earth oxides mixture: i) 6%, j) 7% and k) 10%.](image2)

Fig. 3: Diffraction of ray-X for the zirconias doped with yttrium and of rare earth oxides mixture: i) 6%, j) 7% and k) 10%.
In the Fig. 3 it is shown the diffractions of ray-X for the concentrations of 6%, 7% and 10% of yttrium and of rare earth oxides mixture (curves i), j) and k)). we can observe, based on the Miller index, that in the concentration of 6% of yttrium and of rare earth oxides mixture ( curves i) the predominant phase is the tetragonal, but the measure that we increased the concentration of yttrium and rare earth oxide mixture some picks of the phase tetragonal is going decreasing, as it is the case of the picks whose reflections are indexed as [002], [202], [113], [131] and [004]. besides these there is the increase of the picks [200], [220] and the emergence of the pick [311]. Or be in agreement with the increase of the dopantes concentrations, above 6% of yttrium and of rare earth oxides mixture, the crystalline structure of the zirconia is tending of tetragonal for cubic. These results are proven for the refinement of the lattice parameters, shown in the Fig. 4.

![Graph](image)

Fig. 4: (a) lattice Parameter the versus concentration of yttrium and rare earth oxide mixture in the zirconia and (b) lattice Parameter c versus concentration of yttrium and rare earth oxide mixture in the zirconia

In the Fig. 4 (a) we can observe the evolution (increase) of the lattice parameter \(a\) for the concentrations of 6%, 7% and 10% of yttrium and of rare earth oxides mixture. This increase in the lattice parameter is coherent, because if the lattice parameter the this tending for the cubic phase this will have to increase to equal to the lattice parameter \(c\).

![Graph](image)

Fig. 5: Relationship \(c/a\) versus concentration of yttrium and rare earth oxide mixture in the zirconia.
This can be verified in the Fig. 4 (b), where the lattice parameter c the measure that we increased the concentration of yttrium and rare earth oxide mixture decreases. Therefore, the relationship of the lattice parameters c/a will have to tend to 1. The Fig. 5 display that this statement is true, because the measure that we increased the concentration of yttrium and rare earth oxide mixture the relationship c/a decreases. 

Starting from these results we can prove that most of the elements that it composes the yttrium and rare earth oxide mixture are contributing in a significant way in the stabilization of the zirconia. If this was not true, and basing on the diagram of phase zirconia/yttrium, we would need a very larger proportion of yttrium and of rare earth oxides mixture for the stabilization of the zirconia.

**Conclusion**

With the present work we can conclude that the yttrium and rare earth oxide mixture can be used as stabilization material of the zirconia. Being varied the concentrations of yttrium and rare earth oxide mixture can obtain partially stabilized zirconia with different proportions of phase monoclinic and tetragonal, tetragonal zirconia polycrystals and cubic zirconia. And with 6% of zirconia were obtained the tetragonal zirconia polycrystals.

**References**