Synthesis and characterization of Zirconia-Yttria nanoparticles in t’ phase by sol-gel and spray drying

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Abstract
The synthesis of Zirconia-Yttria nanoparticles in phase t’, non-transformable tetragonal phase of the zirconia, is important for the reinforcement of different ceramic matrices with nanometric and submicronic structures, in order to enhance the mechanical resistance of the composite obtaining a better and homogeneous stress distribution. The objective of this research is to obtain the phase t’ by sol-gel synthesis and spray drying of the gel suspension. The precursors used in this study were: zirconium oxychloride octa-hydrate and yttrium oxide which was dissolved in hydrochloric acid and water, after salts hydrolysis, the suspension subsequently undergo to spray drying and the obtained spherical nanostructured aggregates were calcined at 650 °C. Non transformable tetragonal composition employed was 7.5YSZ (7.5% mol YO1.5), according to the equilibrium diagram of ZrO2-YO1.5 system. The products obtained were characterized by XRD and SEM, verifying obtaining the phase t’ and analyzing the microstructure of the obtained particles. From XRD results, it was determined that calcination temperature was enough for the obtention of the t’ phase. Its results were compared with obtained by controlled precipitation route of the same composition at high temperatures.

Keywords: Yttria stabilized Zirconia nanoparticles, sol gel- spray drying process, non transformable tetragonal phase t’

1. Introduction
It is called the sol-gel process to any process involving a solution or sol that undergoes a transition from sol to gel [1], this technique is one of the most widely used for the synthesis of different ceramic materials [1-4]. Likewise, the sol-gel process used to obtain Yttria stabilized zirconia is very attractive due to its low cost and ease of production at the industrial level [5], especially the synthesis of nano-particles of Zirconia-Yttria in the non-transformable tetragonal phase (t’), since the product is used for the reinforcement of different ceramic matrices with nano-metric and sub-micrometric structures, improving the mechanical strength of the ceramic material, providing a better distribution of the stresses in the compound [6]. The composition range in the ZrO2-YO1.5 system, for which the non-transformable tetragonal phase (t’) is stable, is between 7.5 and 10 mol% of YO1.5 [7]. In the case of thermal barrier coatings in gas turbines, the composition of the phase (t’) used is in the range of 7.6 ± 1 mol% of YO1.5 (7YSZ) [8]. The synthesis of powders in phase t’ is usually carried out with temperatures of calcination exceeding 1000 °C, however, in this research the powders have been treated at lower temperature of 650 °C, after having undergone a process of spray drying, obtaining the tetragonal t’ phase. The volume fraction of the monoclinic phase of the materials synthesized with the sol-gel process with both induced and natural precipitation at temperatures of 1300 °C, 1000 °C and 650 °C were calculated by the expression used by Zhu et al [10], involving the peak intensities t’(111), m(-111) and m(111).

2. Materials and experimental procedure
Zirconium oxychloride octahydrate with 99% purity and yttrium oxide with 99.9% purity were used as raw materials in the synthesis process. The yttrium oxide was dissolved in hydrochloric acid and water. After the salts were hydrolyzed, the suspension was spray-dried and the obtained spherical nano-structured aggregates were calcined at 650 °C, 1000 °C and 1300°C, in an oven at controlled heating temperature. The characteristics of the materials used as raw materials are shown in Table 1.

| Material                          | Purity % | Chemical formula | Molar weight, g/mol |
|-----------------------------------|----------|------------------|---------------------|
| Zirconium oxychloride octahydrate | 99       | ZrOCl2 · 8H2O    | 322.25              |
| Yttrium oxide                     | 98       | Y2O3             | 225.81              |
| Hydrochloric acid                 | -        | HCl              | 36.46094            |
| Water                             | De-ionized | H2O       | 18.01528            |

Table 1. Raw materials used in the synthesis by sol-gel.
1. táblázat A szol-gel szintézis során felhasznált alapanyagok.
Phase identification was performed using the X-ray diffraction (XRD) technique, in a BRUKER equipment, D8 ADVANCE DAVINCHI model of CuKα radiation. The analyses were done using monochromatic X-ray radiation with a graphite monochromator. Scanning from 20 to 85 (2θ) degrees, with a step size of 0.02 degrees and a continuous time per step of 0.06 seconds. Also, microstructure and particle size were analyzed by field emission scanning electron microscopy (FESEM) technique, in a JEOL JSM 7600F microscope. The grinding process of the Yttria stabilized Zirconia was carried out using a planetary ball mill (PBM), RETSCH PM 100 model, maximum capacity in volume of 500 ml and speed of 650 RPM, with possibility of rotation in both senses. 3/8” ball diameter was used for this study.

Yttria-stabilized Zirconia, doped at x mole% YO₁.₅ (x = 7.5) in its non-transformable phase t', was synthesized by the sol gel technique. The resultant suspension was subjected to spray drying with a higher and lower degree of precipitation, resulting in two types of suspensions: with induced precipitation and with natural precipitation. In order to determine the calcination temperature, the thermal treatment was carried out at three calcination temperatures, 650 °C, 1000 °C and 1300 °C, evaluated thereby. The degree of sintering, the particle size, as well as the volume fraction of the monoclinic phase were estimated from SEM and XRD results.

2.1. Sol-gel technique with induced precipitation

Yttrium oxide was first dissolved with hydrochloric acid and water at a temperature of 70 °C, on the other hand, the zirconium oxychloride was dissolved with water for 15 minutes and then both solutions were added with continuous stirring, then 25% by weight of ammonium hydroxide was added dropwise to avoid agglomeration and monitoring the pH, keeping the pH approximately at 7. The suspension was subjected to spray drying process, and then the sample was subjected to heat treatment at 1000 °C and 1300 °C for one hour. In both cases the heating rate was 5 °C/min [6].

2.2. Sol-gel technique with natural precipitation

In this process, after dissolving both salts in water, the solution was spray-dried and the obtained powder was subjected to heat treatment at 650 °C, 1000 °C and 1300 °C. The heat treated sample at 650 °C was maintained for 10 hours and for the samples treated at 1000 °C and 1300 °C for only one hour, maintaining in both cases the heating rate at 5 °C per minute. At low temperature, above 300 °C, the transformation of the amorphous phase into the meta-stable tetragonal phase is presented. Although this phase is stable at temperature range between 1100 °C and 2370 °C, it is obtained at low temperature due to the great loss of structural water from the amorphous [9].

After the synthesis of ZrO₂ stabilized with Yttria, the morphology and phase composition were studied by SEM and XRD.

The products synthesized with heat treatment at 650 °C were characterized by XRD and SEM, to verify the stability of the t’ phase, the degree of sintering and the particle size. The powder obtained after spray drying was subjected to a milling process by PBM with the following milling parameters: weight ratio between balls and sample of 3:1, speed of 200 rpm and time of 5 hours, obtaining a nano-metric particle size. After the grinding process the powders were again characterized by XRD and SEM. After grinding the obtained powder was subjected to a second thermal treatment, at the same conditions, in order to diminish the amount of monoclinic phase. The methodological process for the synthesis of Yttria-stabilized Zirconia in t’ phase with heat treatment at 650 °C and nano-metric particle size, can be observed in Fig. 1.

3. Results and discussion

Fig. 2 shows the diffraction pattern of samples with composition of YSZ with 7.5% mol YO₁.₅ obtained from sol-gel synthesis with and without induced precipitation; In both cases, calcinated samples at 1000 °C and 1300 °C for 1 hr. This pattern corresponds to the tetragonal non-transformable phase called t’, which is confirmed with detail in the range of 70 to 77 degrees of 2 Theta, where the characteristic reflexions of planes (004)t’ and (400)t’ are present, which differentiate this phase with the cubic [6]. This composition is very close to the minimum acceptable of Yttria content without present transformation to the monoclinic phase, according to Schaedler et al [7]. On the other hand, the results of XRD of the samples obtained from the synthesis by sol-gel without induced precipitation and at 650 °C with permanence of 1, 5 and 10 hr, are presented in Fig. 3. X-ray diffraction reveals that the desired phase (t’) is obtained by both methods; however, at all calcination temperatures, the monoclinic phase was found, except in samples thermally treated at 1000 °C and 1300 °C and without induced precipitation, as can be seen in Table 2, which shows the volume fraction of the monoclinic phase for all the samples.

| Sample | Zr-10 (before grinding) | Zr-10 (after grinding) | Zr-10 (calcined after grinding) | T-1000-SC | T1000-SC | T1300-SC | T-1300-SC |
|--------|-------------------------|------------------------|--------------------------------|-----------|---------|---------|---------|
| Monoclinic phase volume fraction (%) | 5.5 | 42.7 | 9.5 | 4.3 | 0 | 2.1 | 0 |

Table 2. Monoclinic phase volume fraction for the different samples.

In Table 2 it can be seen that the t’ phase of the sample calcinated at 650 °C under a low energy milling process presented a transformation to the monoclinic phase, increasing...
the volume fraction of the monoclinic phase of 5.5% to 42.7%. It can be deduced from the above that if a calcined sample at a higher temperature is subjected to a grinding process, it would be necessary to increase the energy supplied in the process to obtain the nano-metric particle size. This is due to the formation of sintering necks, as it is shown in Figs. 4 and 5. It is also observed that for the synthesis processes natural precipitation and calcinated at 1000 °C and 1300 °C, the monoclinic phase does not appear, in addition to presenting a higher degree of sintering, due to a more homogeneous distribution of the salts and the lower diameters of the first products of condensation, than in the case of the synthesis with induced precipitation. In this case, it is evident that more grinding energy is required to obtain the nano-metric size.

Figs. 4 and 5 show the morphology of the powders obtained by spray-drying and calcined at 1000 °C and 1300 °C. It can be observed the nano-metric particle size developed from spray drying and partially sintered by the calcination process. A difference in morphology of the calcination products is also observed because by the sol-gel method with natural precipitation produce a mostly packaged material, with a higher degree of sintering. Whereas by the sol-gel with induced precipitation a material with lower degree of sintering was obtained (Fig. 5). Hardened powders were obtained at both calcination temperatures, 1000 °C and 1300 °C, in both processes, sol-gel with natural precipitation and sol-gel with induced precipitation. It can be concluded that the homogeneity in the solution and smaller size of the first condensation products for the process with natural condensation are important factors that improve densification and optimize the sintering process.

In the case of samples synthesized by the sol-gel process with natural precipitation and calcined at 650 °C, phase t’ was also obtained, but with monoclinic phase formation, unlike samples calcined at higher temperature with the same process, SEM micrographs show that the formation of necks by partial...
sintering is lowest at low temperature Fig. 6, which indicates that this material is going to be easier for grinding than the calcinated one at higher temperature, however, a larger volume fraction of the monoclinic phase is observed when subjected to the grinding process presents transformation of the tetragonal phase to the monoclinic phase after 10 hours at 650 °C after the grinding process, again recovering part of the tetragonal phase, however, the increase in the volume fraction of the monoclinic phase after the grinding process, before and after calcination, was higher than 70%, as shown in Table 2.

4. Conclusions

It was possible to obtain the metastable non-transformable tetragonal phase of Yttria stabilized Zirconia (t’) by means of the sol-gel synthesis process, with natural condensation and at a temperature of 650 °C, thereby facilitating the grinding process to obtain the nano-metric particle size, on the other hand, the better homogeneity obtained in the solution by the process and the lower size of the first condensation products of synthesis with natural condensation contributes with an important way in obtaining the nano-metric particle size, in addition to optimizing the sintering process. The effect generated by milling on ZrO2 powders stabilized with Yttria (t’) is linked to the tetragonal to monoclinic phase transformation even at low milling speeds, which may be directly related to the low calcination temperature at which this t’ Yttria stabilized Zirconia was synthesized.

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Cirkónium-ittrium nanorészécskék szintezése és jellemzői t’ fázisban, szol-gél technikával előállítva

A cirkónium-ittrium nanorészécskék szintezése t’ fázisban (nem transzformálható cirkónium fázis) kiemelt jelentőségű a kerámia mátrixok szubmikron és nano szintű erősítéséhez, a mechanikai jellemzők javításához és a homogénbe feszültségeloszlás eléréséhez a kompozitban. Jelen cikk bemutatja a kutatási eredményeket a t’ fázis előállításához szól-gél technikával. A felhasznált prekurorokon: cirkónium oxiklorid okta-hidrat és ittrium oxid, melyek sósavarban és vízen feloldva, a só hidrolizist követően, szuszpenziók alkotnak, majd a beszáradt gőm alakú nanorészecskék kalcinálása 650 °C hőmérsékleten történik. A kialakuló nem transzformálható tetragonalis fázis 7.5YSZ (7.5 mol% Y2O3) volt, az ZrO2-Y2O3 rendszer egyensúlyi fázisdiagramja alapján. A kapott termékek röntgendiffraktográfiai és százszorosuló elektronmikroszkóppal vizsgálták, amelyekkel azonosították a t’ fázis meglétéét és meghatározották a kialakuló rétegjellemzők jellemzőit. A röntgendiffraktográfiai vizsgálatok igazolták a t’ fázis meglétéét és meghatározották a kialakuló rétegjellemzők jellemzőit. A röntgendiffraktográfiai vizsgálatok igazolták a t’ fázis meglétéét és meghatározották a kialakuló rétegjellemzők jellemzőit.

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Fig. 6. Evolution of the 7YSZ phase in the process of calcination and grinding:

- a) powder calcined for 10 hr at 650 °C after spray drying.
- b) powder obtained with milling for 5 hr at 250 rpm and ball diameter of 3/8”.
- c) nano-metric powder recovered by elutriation process after second calcination process at 10 hr.

6. ábra A 7YSZ fázis fejlődése a kalcinálási és őrlési folyamatok során:

- a) Por 5 órás őrlést követően 250 rpm fordulatszámon 3/8” őrlőgolyókkal.
- b) Por 10 órás 650 °C kalcinálást követően.
- c) Nano-metric powder recovered by elutriation process after second calcination process at 10 hr.