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

Gerardo Manuel RODRÍGUEZ TORRES ▪ Instituto de Investigación en Metalurgia y Materiales, Universidad Michoacana de San Nicolás de Hidalgo ▪ rodriguezg671124@hotmail.com
Juan ZARATE MEDINA ▪ jzarate@umich.mx
María Eugenia CONTRERAS GARCÍA ▪ eucontre@gmail.com

Érkezett: 2016. 11. 02. ▪ Received: 02. 11. 2016. ▪ http://dx.doi.org/10.14382/epitoanyag-jsbcm.2016.21

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 matrixes with nanometric and submicronic structures, in order to enhance the mechanical resistance of the composite obtaining a better and homogeneus 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 $YO_{1.5}$), according to the equilibrium diagram of ZrO_2-$YO_{1.5}$ 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'

Gerardo Manuel RODRÍGUEZ TORRES
MSc since 1997, PhD student at the Universidad Michoacana de San Nicolás de Hidalgo (UMSNH) since 2015, Title of PhD work is "Influence of the Addition of Stabilized Zirconia Particles in the Mechanical Properties of Micro Concretes made with Submicrometric Portland Composite Cement". Teaching Experience: Introduction to Materials Science, Construction Materials and Road Construction Workshop. Work Experience: Manager of project in the company impact engineering of quality SA de CV Mexico, with more than 150 executive projects in road infrastructure area in period 2006-2013.

Juan ZARATE MEDINA
Lecturer and Researcher, research interests: Synthesis and Processing of Ceramics and Compounds, and Materials Characterization, Work Experience: Titular Researcher C, at "Universidad Michoacana de San Nicolás de Hidalgo", UMSNH, since 2002. MSc Program Coordinator from 2009 to 2011, PhD Program Coordinator since 2015. Publications: 30+ publications in JCR Journals in the field of Ceramics Materials and Composites. Graduated supervisor: 12 MSc and 2 PhD thesis in the UMSNH.

María Eugenia CONTRERAS GARCÍA
Doctor of Sciences since 2000, Titular C Professor and Researcher at the Ceramic Materials Department of the Metallurgy and Materials Research Institute on the Universidad Michoacana de San Nicolás de Hidalgo since 1988 and Level 2 National Researcher since 2001. Specialized on Ceramic Synthesis and Processing Techniques such as ceramic powder processing via sol-gel and chemical techniques, focused on nanostructured ceramics processing and functional ceramics including: structural ceramics, bioceramics, magnetic ceramics, optoelectronic ceramics, catalytic and photocatalytic ceramics, macro-mesoporous ceramics all of them in bulk and in thin films. She is author and co-author of more than 100 international indexed papers, two book chapters and editor in one. She is member of several scientific societies and regional director of the Mexican Academy of Crystallography.

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 ZrO_2-$YO_{1.5}$ system, for which the non-transformable tetragonal phase (t') is stable, is between 7.5 and 10 mol% of $YO_{1.5}$ [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 mole% of $YO_{1.5}$ (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	$ZrOCl_2 \cdot 8H_2O$	322.25
Yttrium oxide	98	Y_2O_3	225.81
Hydrochloric acid	-	HCl	36.46094
Water	De-ionized	H_2O	18.01528

Table 1. Raw materials used in the synthesis by sol-gel.
1. táblázat A szol-gél 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% $YO_{1.5}$ (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-dryed 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 ZrO_2 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*.

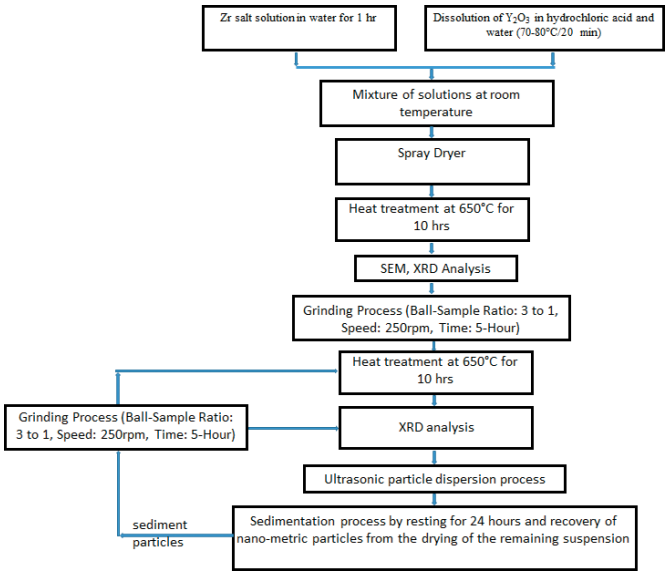

Fig. 1. Experimental procedure diagram for synthesis, grinding and characterization of Zirconia stabilized with Yttria in phase t' at 650°C of heat treatment [9]
1. ábra Kísérleti eljárási diagram cirkóniummal stabilizált ittrium t' fázis szintéziséhez, őrléséhez, jellemzéséhez, 650 °C hőkezelés esetén [9]

3. Results and discussion

Fig. 2 shows the diffraction pattern of samples with composition of YSZ with 7.5% mol $YO_{1.5}$ 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-C	T1000-SC	T1300-C	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.
2. táblázat Monoklin fázis térfogatarányа a különböző mintákban.

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.

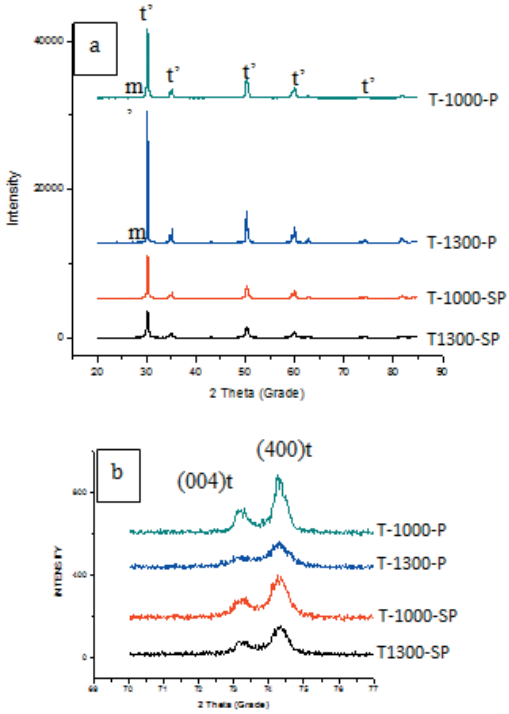

Fig. 2. Yttria stabilized Zirconia in phase t', synthesized by the sol-gel technique with and without condensation process, calcined at 1000 °C and 1300 °C.
a) Diffraction pattern of phase t' of Zirconia stabilized with Yttria.,
b) Detail in the range of 70° - 77° of 2Theta
2. ábra Ittriummal stabilizált cirkónium t' fázis; szol-gél szintézis, kondenzálással és anélkül, kalcinálás 1000 °C és 1300 °C hőmérsékleten.
a) A t' fázis röntgendiffraktogramja
b) Diffraktogram részlet 70° - 77° 2Theta értékek között

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.

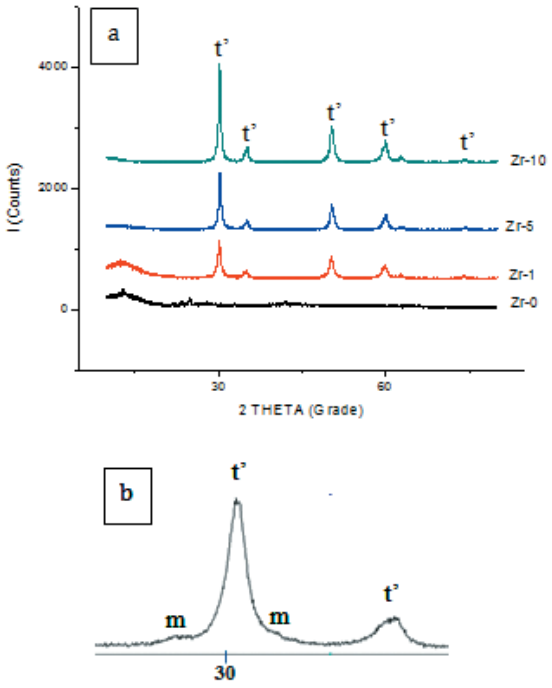

Fig. 3. a) Yttria stabilized Zirconia in phase t', synthesized by sol-gel technique without condensation and calcined at 650 °C with permanence of 1, 5 and 10 hr, b) detail between 26° and 35° of 2Theta For Zr-10
3. ábra a) Ittriummal stabilizált cirkónium t' fázis; szol-gél szintézis, kondenzálás nélkül, kalcinálás 650 °C hőmérsékleten, 1, 5 és 10 óra időtartammal
b) Zr-10 diffraktogram részlete 26° - 35° 2Theta értékek között

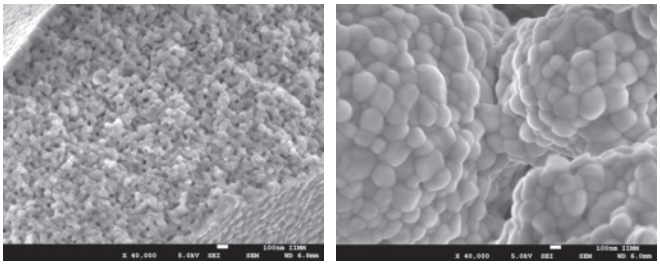

Fig 4. Yttria stabilized Zirconia in phase t' morphology, synthesized by sol-gel technique without condensation, calcined at a) 1000 °C and b) 1300 °C. SEM
4. ábra. Ittriummal stabilizált cirkónium t' fázis morfológiája (SEM); szol-gél szintézis, kondenzálás nélkül, kalcinálási hőmérséklet a) 1000 °C és b) 1300 °C

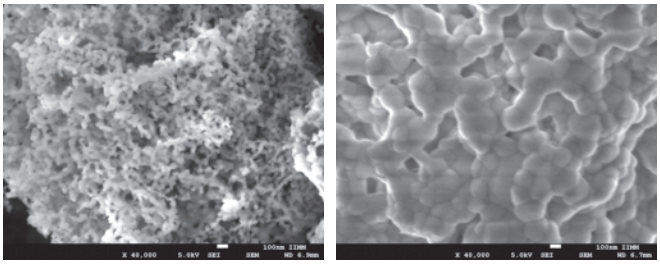

Fig 5. Yttria stabilized Zirconia in phase t', synthesized by the sol-gel technique with condensation: a) 1000 °C and b) 1300 °C. SEM
5. ábra Ittriummal stabilizált cirkónium t' fázis; szol-gél szintézis, kondenzálás nélkül, kalcinálási hőmérséklet a) 1000 °C és b) 1300 °C (SEM)

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, having to be subjected to thermal treatment for 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*.

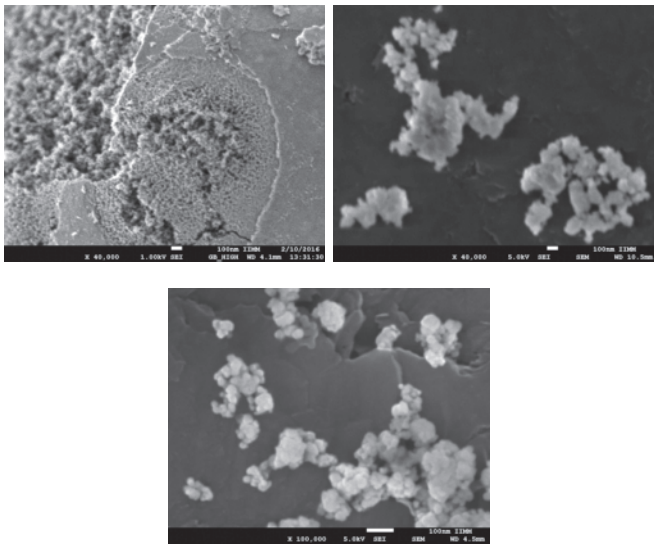

Fig 6. Evolution of the 7YSZ phase in the process of calcination and grinding:
a) powder calcined for 10 hr at 650 °C after spray drying,
b) powder obtained with milling for 5 hr at 250 rpm and ball diameter of 3/8"
c) nano-metric powder recovered by elutriation process after second calcination process at 10 hr

6. ábra A 7YSZ fázis fejlődése a kalcinálási és őrlési folyamatok során
a) Por 10 órás 650 °C kalcinálást követően
b) Por 5 órás őrlést követően 250 rpm fordulatszámon 3/8" őrlőgolyókkal
c) Nano-méretű szemcsék a második 10 órás kalcinálást követően

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 ZrO_2 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.

5. Acknowledgements

The authors acknowledge the financial support for this research provided by the Consejo Nacional de Ciencia y Tecnología (CONACYT) and CIC-UMSNH.

References

[1] Klein, L. C. (1985): Sol-Gel Processing of Silicates. *Annual Review of Materials Science*. Vol. 15, pp. 227-248. http://dx.doi.org/10.1146/annurev.ms.15.080185.001303

[2] Aguilar, D. H. – Torres-Gonzalez, L. C. – Torres-Martinez, L. M. (2000): A Study of the Crystallization of ZrO_2 in the Sol-Gel System: ZrO_2+SiO_2. *Journal of Solid State Chemistry*. Vol. 158, No. 2, pp. 349-357 http://dx.doi.org/10.1006/jssc.2001.9126

[3] Cho, S. B. – Kim, S. B. – Cho, K. J. – Ohtsuki, C. – Miyazaki, T. (2004): Development of Novel PMMA-Based Bone Cement Reinforced by Bioactive CaO-SiO2 Gel Powder. *Key Engineering Materials*. Vols. 254-256, pp. 285-288, http://dx.doi.org/10.4028/www.scientific.net/KEM.254-256.285

[4] Cho, S. B. – Kim, S. B. – Cho, K. J. – Kim, I. Y. – Ohtsuki, C. – Kamitakahara, M. (2005): In vitro aging test for bioactive PMMA-based bone cement using simulated body fluid. *Key Engineering Materials*. Vols. 284–286, pp.153-156 http://dx.doi.org/10.4028/www.scientific.net/KEM.284-286.153

[5] Viazzi, C. – Bonino, J-P. – Ansart, F. – Barnabé, A. (2008): Structural study of metastable tetragonal YSZ powders produced via a sol–gel route. *Journal of Alloys and Compounds*. Vol. 452, No. 2, pp. 377–383, http://dx.doi.org/10.1016/j.jallcom.2006.10.155

[6] Danna Lizeth Trejo Arroyo (2015): Síntesis y procesamiento de medios de molienda de alúmina reforzada con zirconia a partir de pseudoboehmita sembrada in-situ con semillas de α-alúmina. IIM, UMSNH, Tesis Doctoral. 47 p.

[7] Schaedler, T. A. – Leckie, R. M. – Krämer, S. – Evans, A. G. – Levi, C. G. (2007): Toughening of Non-Transformable t'-YSZ by Addition of Titania. *Journal of the American Ceramic Society*. Vol. 90, No. 12, pp. 3896-3901, http://dx.doi.org/10.1111/j.1551-2916.2007.01990.x

[8] Stecura, S. (1985): Optimization of the NiCrAl-Y/ZrO_2-Y_2O_3 thermal barrier system. *NASA Report* No. TM-86905 1985, Cleveland, OH.

[9] Rashad, M. M. – Baioumy, H. M. (2008): Effect of thermal treatment on the crystal structure and morphology of zirconia nanopowders produced by three different routes. *Journal of Materials Processing Technology*. Vol. 195, No. 1-3, pp. 178–185, http://dx.doi.org/10.1016/j.jmatprotec.2007.04.135.

[10] Zhu, C. – Li, P. – Javed, A. – Liang, G. Y. – Xiao, P. (2012): An investigation on the microstructure and oxidation behavior of laser remelted air plasma sprayed thermal barrier coatings. *Surface & Coatings Technology.* Vol. 206, No. 18, pp. 3739–3746, http://dx.doi.org/10.1016/j.surfcoat.2012.03.026

Ref.:
Rodríguez Torres, Gerardo Manuel – **Zarate Medina**, Juan – **Contreras García**, María Eugenia: *Synthesis and characterization of Zirconia-Yttria nanoparticles in t' phase by sol-gel and spray drying*
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 68, No. 3 (2016), 120–123. p.
http://dx.doi.org/10.14382/epitoanyag-jsbcm.2016.21

Cirkónium-ittrium nanorészecskék szintézise és jellemzői t' fázisban, szol-gél technikával előállítva

A cirkónium-ittrium nanorészecskék szintézise t' fázisban (nem transzformálható tetragonális cirkónium fázis) kiemelt jelentőségű a kerámia mátrixok szubmikron és nano szintű erősítéséhez, a mechanikai jellemzők javításához és a homogénebb feszültségeloszlás eléréséhez a kompozitban. Jelen cikk bemutatja a kutatási eredményeket a t' fázis előállításához szol-gél technikával. A felhasznált prekurzorok: cirkónium oxiklorid okta-hidrát és ittrium oxid, melyek sósavban és vízben feloldva, a só hidrolízist követően, szuszpenziót alkotnak, majd a beszáradt gömb alakú nanorészecskék kalcinálása 650 °C hőmérsékleten történik. A kialakuló nem transzformálható tetragonális fázis 7.5YSZ (7.5% mol $YO_{1.5}$) volt, az ZrO_2-$YO_{1.5}$ rendszer egyensúlyi fázisdiagramja alapján. A kapott termékeket röntgendiffrakcióval és pásztázó elektronmikroszkóppal vizsgálták, amelyekkel azonosították a t' fázis meglétét és meghatározták a kialakult részecskék jellemzőit. A röntgendiffrakciós vizsgálat igazolta, hogy az alkalmazott kalcinálási hőmérséklet elégséges a t' fázis kialakulásához.

Kulcsszavak: ittriummal stabilizált cirkónium-oxid nanorészecskék, szol-gél technológia, nem transzformálható tetragonális t' fázis