SYNTHESIS AND MECHANICAL PROPERTIES OF STABILIZED ZIRCONIA CERAMICS: $MgO-ZrO_2$ and Y_2O_3-MgO- ZrO_2

C. Yamagata[1, a], S. R. H. Mello-Castanho[1, b] J. O. A. Paschoal[1, c]

[1]Instituto de Pesquisas Energéticas e Nucleares, Centro de Ciência e Tecnologia de Materiais (CCTM), Av. Prof. Lineu Prestes, 2242, CEP-05508-000, Universidade de São Paulo, São Paulo, SP, Brazil.

[1, a]yamagata@ipen.br, [1,b]srmello@ipen.br,[1,c]paschoal@institutoinova.org.br

Keywords: $MgO-Y_2O_3-ZrO_2$, synthesis, microstructure, hardness

Abstract. Precursor $MgO-ZrO_2$ and Y_2O_3-$MgO-ZrO_2$ ceramic powders were synthesized by the method of co-precipitation and characterized by techniques such as laser diffraction, QELS (Quasi Elastic Light Scattering), XRD, BET, and SEM. Nanoscale powders with specific surface area higher than 60 $m^2. g^{-1}$ was achieved. Sintered ceramic obtained from the synthesized powders, were characterized to mechanical tests using Vickers indentation technique. The addition of Y_2O_3 promoted an increase in hardness of the ceramics and total cubic crystalline phase stabilization.

Introduction

Yttria-Magnesia-Zirconia system (Y_2O_3-$MgO-ZrO_2$) is a promising material to producing refractory materials with high mechanical properties. In appropriate compositions, its mechanical property resists even subjected to high temperatures. The toughness of $MgO-ZrO_2$ ceramic system is mainly induced by the mechanism of the tetragonal to monoclinic transformation[1] of tetragonal metastable precipitates confined in cubic phase. However, at high temperatures, this ceramic suffer the decomposition[2] of tetragonal and cubic phases in to monoclinic and magnesia. The addition of yttria in the $MgO-ZrO_2$ system inhibits this decomposition and promotes an improvement in mechanical and electrical properties of the ceramic. Therefore, the study of the synthesis and characterization of the Y_2O_3-$MgO-ZrO_2$ system is interesting to develop new materials with enhance properties by zirconia stabilization. Various methods are proposed to synthesize those materials, such as: mixture of oxide powders procwdure[3], method of citrates[4] precipitation[5] and sol gel[6] techniques. In this paper MgO stabilized zirconia powders were prepared with Y_2O_3 addition by co-precipitation method[7]. The morphology and particle size distribution of the powders as well as crystalline phases and specific surface area were characterized. The ceramic obtained from synthesized powders were submitted to mechanical testing using Vickers indentation technique[8].

Experimental

Starting materials were consisted of magnesium chloride ($MgCl_2$), yttrium chloride (YCl_3) and zirconium oxychloride ($ZrOCl_2$) obtained by dissolution of magnesium hydroxide, yttrium oxide and zirconium hydroxide in hydrochloric acid, respectively. Hydroxides of magnesium, zirconium and yttrium were co-precipitated under optimized conditions[7] to obtain precursor powders of $MgO-ZrO_2$ and Y_2O_3-$MgO-ZrO_2$. Precursor solution was prepared by mixing the starting materials in the proportion of ZrO_2 : MgO: Y_2O_3, formerly defined. This precursor solution was dropped in ammonium hydroxide solution, in a previous calculated volume according to the optimal relationship $[OH^-]/[Cl^-]$ equal to 4.4[7]. The ammonia solution was vigorously stirred during the whole precipitation process. The obtained co-precipitate, consisted of magnesium, zirconium and yttrium hydroxides, was separated by vacuum filtration, washed with distilled water for removal chloride ions, which was checked by the silver chloride test. After washing with water, the co-

precipitate was washed with ethanol, separated by vacuum filtration; oven dried and calcined in muffle at 500 ^{o}C for 1h. After that, the obtained product has been grinding in ethanol in high-energy milling for 4h. Resulted powders were characterized; the particle size distribution by laser diffraction QELS (Quasi Elastic Light Scattering), the specific surface area by the BET method, the morphology of the clusters were observed by SEM and crystallinity determined by XRD. Y_2O_3-MgO-ZrO_2 ceramics pellets were prepared from synthesized powders by uniaxial compression with 98 MPa pressure, and sintered at 1500 ^{o}C for 1h. Those sintered pellets were submitted to the mechanical characterization. Vickers test was performed to evaluate the mechanical properties (hardness and fracture toughness), of the ceramic. The Vickers print test consists of applying a load through a diamond penetrator in the material and measure of the cracks produced, which is direct function of indentation load[8]. Sintered samples were cut into longitudinal direction with a diamond disk, embedded in *bakelite,* polished with diamond suspensions of diameter size, 15, 6 and 1μm, in automatic *polishing machine*. After polishing, the samples were submitted to the test in *Buehler VMT-7*, which is endowed with a penetrator with diamond prism of square base. The test was consisted of applying, with the penetrator, a perpendicular load on the surface of the sample and subsequent measurement of the penetrator printing (Vickers printing). The load application time was 15 seconds. About 10 Vickers impressions were made in each sample, observing the distance between the centers of the impressions, of approximately four lengths of cracks generated, as well as the distance in relation to the edge of the sample[9]. Preliminary tests were carried out on the samples, varying the load of 10 to 100 N, for the definition of load of the penetrator. In this step, it was found that the trips generated at practice were the Palmqvist type[10]. For the determination of fracture toughness using the equation[8, 11] suitable for trips of type Palmqivst.

Results and discussion

The molar composition of co-precipitated Y_2O_3-MgO-ZrO_2 samples is listed in Table 1.

Table 1 – Molar composition of Y_2O_3 -MgO- ZrO_2 samples

Sample	[MgO]/[OT]* (mol %)	[Y_2O_3]/[OT] (mol %)	{[MgO] + [Y_2O_3]}/[OT] (mol %)	[Y_2O_3]/[MgO] (mol %)
MZ	7.8	0	7.8	0
YMZ	7.4	2.4	9.8	24.9

* [OT] = [ZrO_2] + [MgO] + [Y_2O_3]

In Fig. 1 there are the analysis results of MZ and YMZ samples particle size distribution, after calcining the powders at 550 ^{o}C for 1h and grinding in high-energy ball milling, for 4h. From the particle size distribution curves shown in Fig. 1, samples are consisted of very fine medium-sized clusters in the range of 20 to 30 nm.

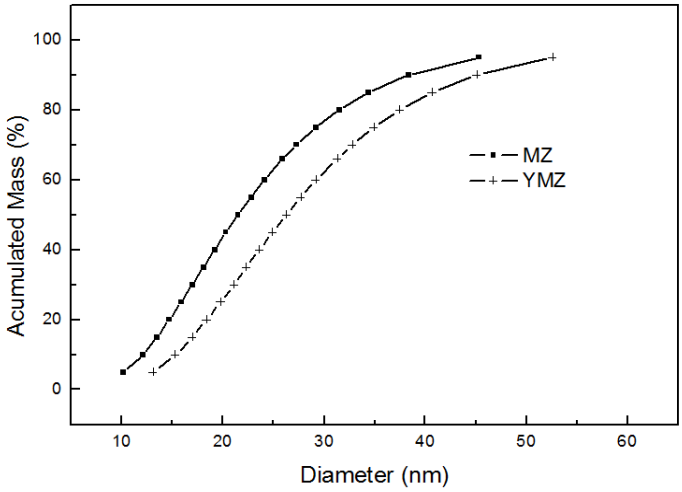
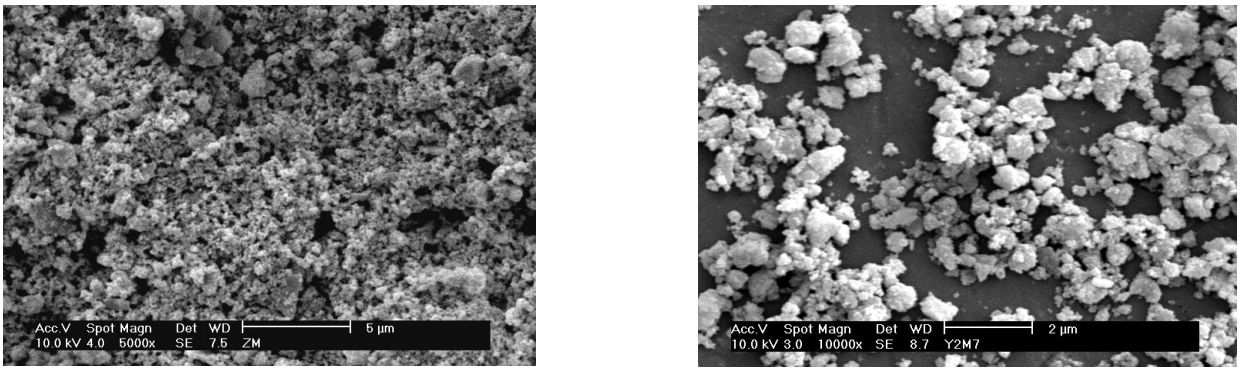


Figure 1- MZ and YMZ samples particle size distribution, after calcining the powders at 550 ^{o}C for 1h and grinding in high-energy ball milling, for 4h.

The micrographs of the samples MZ and YMZ calcined at 550 ^{o}C obtained by SEM are shown in Fig. 2. It is observed the presence of clusters of rounded morphology with fine particles, agreeing with the results of particle size distribution analysis exposed in Fig. 1.



(A) (B)

Figure 2-Micrographs obtained by SEM of the MZ samples (A) and (B) YMZ calcined at 550 ^{o}C for1h.

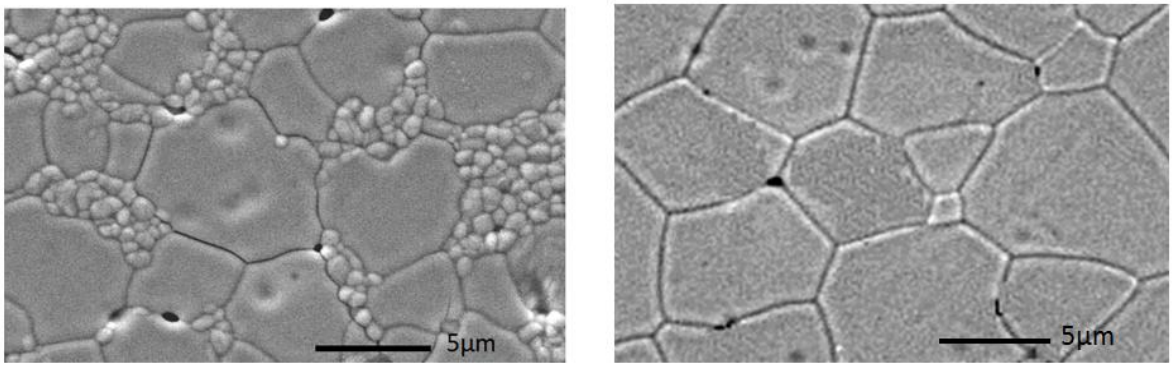
It is verified the specific surface area, obtained by BET method, listed in Table 2 are high, revealing that the prepared powders have good reactivity and point toward a consistency with fine particulates presented in Fig. 2 (A) and Fig. 2 (B).

Table 2 – specific surface area determined by the BET method of the samples calcined at 550^{0}C

Sample	Specific surface area ($m^2 g^{-1}$)
MZ	64.8
YMZ	70,1

In Fig. 3 micrographs obtained by SEM from polished surface of the samples, MZ and YMZ are shown. In Fig. 3 (A) a typical microstructure of ceramics ZrO_2-MgO type is observed, including

grains of c-ZrO_2 (larger) and m-ZrO_2 (minors). For these ceramics, the average size of the grains of c-ZrO_2 is approximately 5.5 μm and 1.5 μm for m-ZrO_2[12], these dimensions can be seen in Fig. 3 (A). In Fig 3(B), grains of c-ZrO_2 are only observed, with size greater than 5μm.



(A) (B)

Figure 3- Micrographs obtained by SEM from polished surface of the samples, MZ and YMZ

XRD patterns of the sintered samples are presented in Fig. 4 and Fig. 5. In the sample MZ (Fig. 4) it is observed the majority of c-ZrO_2 (cubic phase of zirconia) and minor of m-ZrO_2 (monoclinic phase zirconia), verified by the reflections of the plans m (-111) and m (111). In the sample YMZ, XRD peaks of m-ZrO_2 are not noticed. The presence only of c-ZrO_2 phase agrees with the previous micrograph (Fig. 3 (B)), where the presence of m-ZrO_2 is not shown. Above obtained results are in agreement with the expected because the presence of yttria in the MgO-ZrO_2 system inhibits the formation of m-ZrO_2 phase, by stabilizing the cubic phase[13].

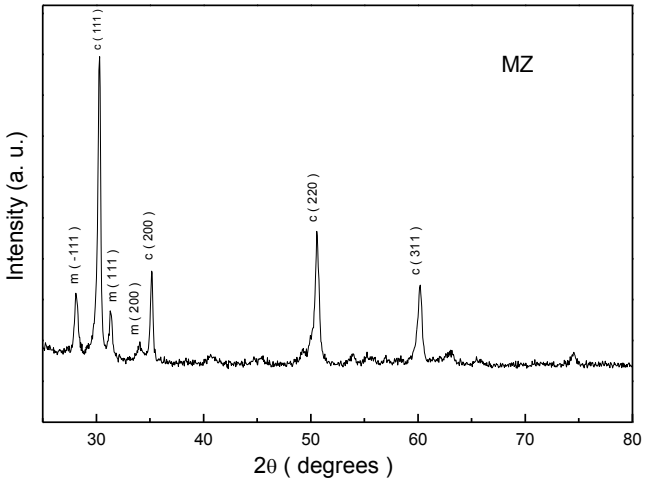


Figure 4-XRD patterns of sample MZ sintered at 1500 ^oC for 1h.

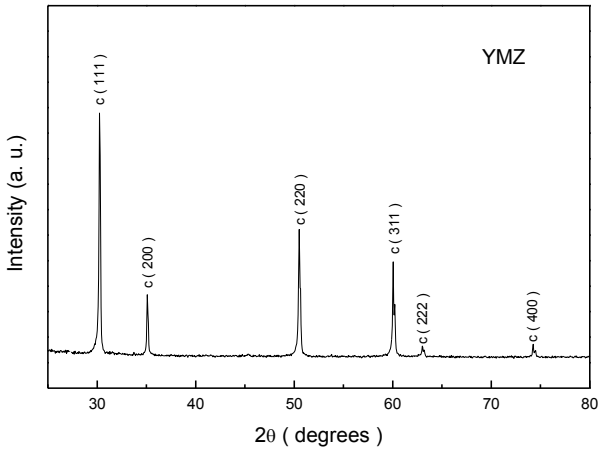


Figure 5-XRD patterns of sample YMZ sintered at 1500 ^{o}C for 1h.

Vickers hardness values (H_v) and fracture toughness (K_{IC}) are shown in Table 3. It is observed hardness has been increased and a decrease in fracture toughness of the material, by the addition of yttria.

Table 3-Values of hardness and toughness of the ceramics samples and MZ and YMZ sintered at 1500 ^{o}C for 1h.

Sample	H_v hardness (GPa)	Fracture toughness K_{IC} (MPa $m^{1/2}$)
MZ	10.90 ± 0.32	6.63 ± 0.51
YMZ	12,04 ± 1,45	3,01 ± 0,31

Comparing the results presented in Table 3, it fits out that the hardness values obtained in this study are consistent with those presented in the literature [12-17]. As mentioned earlier, the tenacity of MgO system ceramics-ZrO_2 depends mainly on the induced transformation mechanism of precipitates tetragonal (t-ZrO_2) confined in metastable cubic arrangement. For the development of these precipitates of t-ZrO_2, it is necessary to heat ageing treatment after sintering. Heat treatment after sintering at temperatures between 1400 and 1500 ^{o}C is very important because the mechanical and electrical properties of stabilized zirconia based ceramics with magnesia, Mg-PSZ, are optimized for this processing[18]. In the present study the subsequent sintering heat treatment was not performed, so the results of mechanical properties of Vickers hardness H_v and fracture toughness K_{IC} can still be increased by this processing. For example, Meschke[19] obtained an increasing in fracture toughness of (Mg-Y)-PSZ ceramics type, i. e., to 11.2 Mpa $m^{1/2}$ from 6.0 Mpa $m^{1/2}$ by heat treatment after sintering.

Conclusions

Precursor powders of Y_2O_3-MgO-ZrO_2 were prepared by precipitation technique. After calcination at 550 ^{o}C and grinding, the powders have average size of clusters between 20 to 30 nm and specific surface is in the range of 60 to 70. $m^2 . g^{-1}$. Those powders after sintering at 1500 ^{o}C for 1h, resulted in ceramics with Vickers hardness (H_v) greater than 10 GPa and fracture toughness (K_{IC}) of 6.63 and 3.01 for Mg-PSZ and (Y-Mg)-PSZ) respectively. XRD analysis revealed that in the both ceramics, c-ZrO_2 crystalline phase is the main. In the sample in which Y_2O_3 was added, monoclinic phase, m-ZrO_2, was not virtually observed.

References

[1] Jing Li, Jinhui Peng, Shenghui Guo, Wenwen Qv, Guo Chen, Wei Li, Libo Zhang pages, Martensitic transformation thermodynamic calculation of ZrO_2–MgO system, Phase Transitions: A Multinational Journal, 85, 11 (2012)1022-1029.

[2] Yu. Prokhorov, Thermal stability of oxide ceramic materials, Ogneupory Tekh. Keram., No. 5 (2002) 36–47.

[3] N. Stubicar, V. Bernanec, M. Stubicar, D. Popovic, W. A. Kaysser, X-ray diffraction study of microstructural evolution of some MgO-Y_2O_3-ZrO_2 powders mixtures minded is life eternal by high-energy ball milling J. Alloys Comp., 379 (2004) 216-221.

[4] M. Yahima, M. Kakina, Synthesis of tetragonal (t) zirconia-calcia solid solution by pyrolysis of organic precursors and coprecipitation route, J. Mat. Res. 11, 6, (1996) 1410-1420.

[5] Sukhen Das, N. K. Mitra, Sudip Das , Sintered Properties and Sintering Behavior of Mgo–Zro2 Composite Hydrogel Prepared by Coprecipitation Technique, Science of Sintering, 44 (2012) 35-45.

[6] T. Settu, Characterization of MgO-ZrO_2 precursor powders prepared by in-situ peptisation of coprecipitated gel oxalate, Ceram. Int., 26(2000) 516-521.

[7] C. Yamagata, Influence of synthesis conditions on the characteristics of precipitation with stabilized zirconia MgO and application in the system MgO-$Zr0_2$-Y_2O_3**.** **(**2004), 162p. Thesis (doctorate in Nuclear Technology-materials) – Energy and nuclear research Institute, Ipen/Cnen-SP, São Paulo.

[8] A. Iost, R. Bigot, Indentation size effect: reality or artifact? , J. Mat. Sci., v. 31, (1996) 3573-3577,

[9] K. Niihara, The fracture mechanics analysis of identation-induced Palmqvist crac in ceramics, J. Mat. Sci. Lett., (1983) 221-223.

[10] K. S. Chan, G. K. Chuah, S. Jaenicke, Preparation of high surface area zirconia, stabilized, J. Mater. Sci. Lett. 13(1994), 1579-1581.

[11] R. C. Garvie, M. F. Goss, Intrinsic size dependence of phase transformation te*m*perature in Crystal arthropathies zirconia, J. Mat. Sci**.**, 21(1986)1253-1257.

[12] J. F. Fue, A. V. Virkar, Fabrication, characterization, microstructural and mechanical properties of polycrystalline t-zirconia, J.Am. Ceram. Soc., 73(1990) 3650-3657.

[13] Q. Zhang, H. Z. Wu, Y. R. Chen, W.X Liu, Q.M. Yuan, Thermal stability and microstructural development of fine-grained (Y-Mg)-PSZ ceramics, J. Eur. Ceram. Soc., 18 (1998) 647-651.

[14] I. Abrahan, G. Gritzner, Mechanical properties of doped cubic zirconia ceramics, J. Mat. Sci. Lett. , 12 (1993), 995-997.

[15] T. Sato, T. Endo, M. Shimada, Hydrothermal corrosion magnesia partially-stabilized zirconia, J. Mat. Sci., 26 (1991) 1345-1350.

[16] J. Duh, H. T. Hence, Sintering, microstructure, hardness, fracture toughness and behavior of Y_2O_3-ZrO_2-CeO, J. am.. Ceam. Soc., 71, 10 (1988), 813-819.

[17] C. S. Montross, Precipitation and bulk property behavior in into-magnesia-zirconia ternary system, Br. Ceram. Trans.J., 90 (1991) 175-178.

[18] R. H.Hannink, Microstructural development of sub-eutectoid aged MgO-ZrO_2 alloys, J. Mat. Sci., 18 (1983) 457-470.

[19] F. Meschke, N. Claussen, G.De Portu, J. Rand, thermal stability and Microstructure of fine-grained (Y-Mg)-PSZ ceramics with alumina additions, J. Eur. Ceram. Soc., 17 (1997) 843-850.