

SYNTHESIS AND MECHANICAL PROPERTIES OF STABILIZED ZIRCONIA CERAMICS: MgO-ZrO₂ and Y₂O₃-MgO- ZrO₂

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Abstract. Precursor MgO-ZrO₂ and Y₂O₃-MgO-ZrO₂ 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 m². g⁻¹ was achieved. Sintered ceramic obtained from the synthesized powders, were characterized to mechanical tests using Vickers indentation technique. The addition of Y₂O₃ promoted an increase in hardness of the ceramics and total cubic crystalline phase stabilization.

Introduction

Yttria-Magnesia-Zirconia system (Y₂O₃-MgO-ZrO₂) 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-ZrO₂ ceramic system is mainly induced by the mechanism of the tetragonal to monoclinic transformation¹ of tetragonal metastable precipitates confined in cubic phase. However, at high temperatures, this ceramic suffer the decomposition² of tetragonal and cubic phases in to monoclinic and magnesia. The addition of yttria in the MgO-ZrO₂ 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 Y₂O₃-MgO-ZrO₂ 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 procedure³, method of citrates⁴ precipitation⁵ and sol gel⁶ techniques. In this paper MgO stabilized zirconia powders were prepared with Y₂O₃ addition by co-precipitation method⁷. 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 technique⁸.

Experimental

Starting materials were consisted of magnesium chloride (MgCl₂), yttrium chloride (YCl₃) and zirconium oxychloride (ZrOCl₂) 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 conditions⁷ to obtain precursor powders of MgO-ZrO₂ and Y₂O₃-MgO-ZrO₂. Precursor solution was prepared by mixing the starting materials in the proportion of ZrO₂ : MgO: Y₂O₃, 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 4.4⁷. 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 °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. Y₂O₃-MgO-ZrO₂ ceramics pellets were prepared from synthesized powders by uniaxial compression with 98 MPa pressure, and sintered at 1500 °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 load⁸. 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 sample⁹. 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 type¹⁰. For the determination of fracture toughness using the equation^{8,11} suitable for trips of type Palmqvist.

Results and discussion

The molar composition of co-precipitated Y₂O₃-MgO-ZrO₂ samples is listed in Table 1.

Table 1 – Molar composition of Y₂O₃ -MgO- ZrO₂ samples

Sample	[MgO]/[OT] [*] (mol %)	[Y ₂ O ₃]/[OT] (mol %)	{[MgO] + [Y ₂ O ₃]}/[OT] (mol %)	[Y ₂ O ₃]/[MgO] (mol %)
MZ	7.8	0	7.8	0
YMZ	7.4	2.4	9.8	24.9

^{*} [OT] = [ZrO₂] + [MgO] + [Y₂O₃]

In Fig. 1 there are the analysis results of MZ and YMZ samples particle size distribution, after calcining the powders at 550 °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.

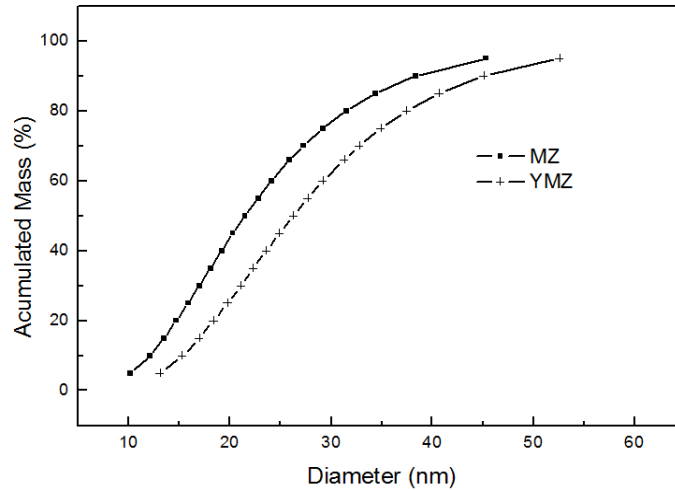
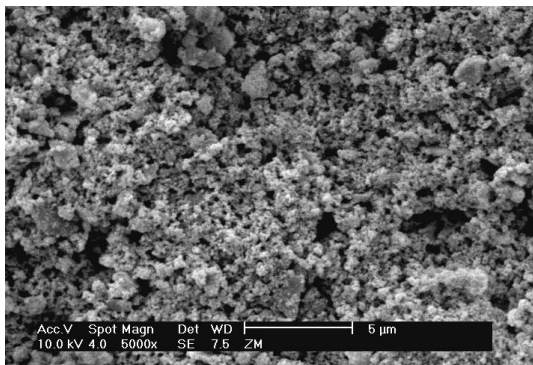
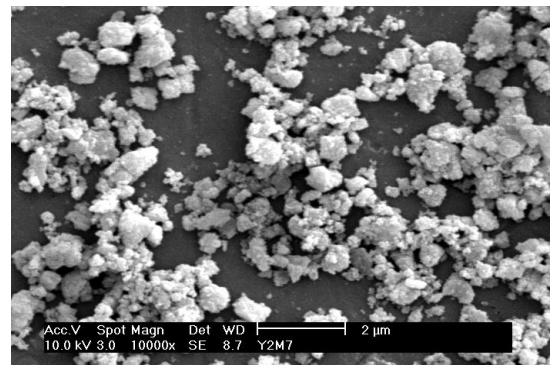


Figure 1- MZ and YMZ samples particle size distribution, after calcining the powders at 550 °C for 1h and grinding in high-energy ball milling, for 4h.

The micrographs of the samples MZ and YMZ calcined at 550 °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 °C for 1h.

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°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 ZrO₂-MgO type is observed, including

grains of c-ZrO₂ (larger) and m-ZrO₂ (minors). For these ceramics, the average size of the grains of c-ZrO₂ is approximately 5.5 μm and 1.5 μm for m-ZrO₂¹², these dimensions can be seen in Fig. 3 (A). In Fig 3(B), grains of c-ZrO₂ are only observed, with size greater than 5μm.

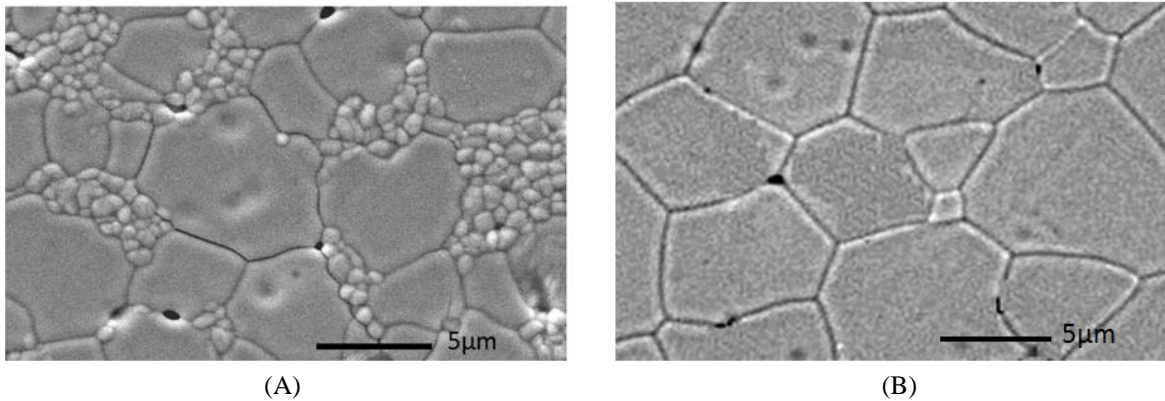


Figure 3- Micrographs obtained by SEM from polished surface of the samples, MZ and YMZ

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-ZrO₂ (cubic phase of zirconia) and minor of m-ZrO₂ (monoclinic phase zirconia), verified by the reflections of the plans m (-111) and m (111). In the sample YMZ, XRD peaks of m-ZrO₂ are not noticed. The presence only of c-ZrO₂ phase agrees with the previous micrograph (Fig. 3 (B)), where the presence of m-ZrO₂ is not shown. Above obtained results are in agreement with the expected because the presence of yttria in the MgO-ZrO₂ system inhibits the formation of m-ZrO₂ phase, by stabilizing the cubic phase¹³.

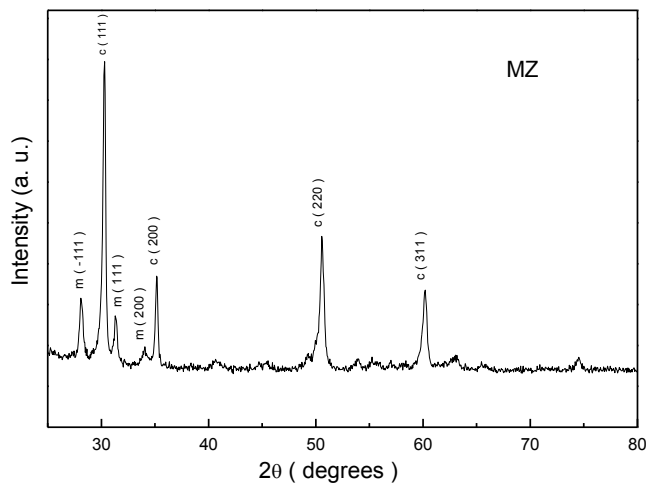


Figure 4-XRD patterns of sample MZ sintered at 1500 °C for 1h.

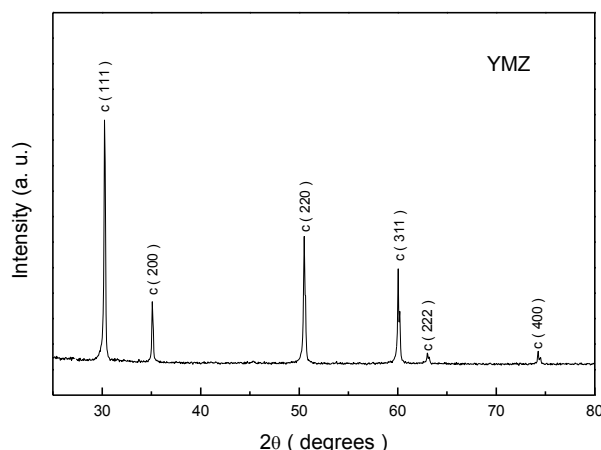


Figure 5-XRD patterns of sample YMZ sintered at 1500 °C for 1h.

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 °C for 1h.

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

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 literature¹²⁻¹⁷. As mentioned earlier, the tenacity of MgO system ceramics-ZrO₂ depends mainly on the induced transformation mechanism of precipitates tetragonal (t-ZrO₂) confined in metastable cubic arrangement. For the development of these precipitates of t-ZrO₂, it is necessary to heat ageing treatment after sintering. Heat treatment after sintering at temperatures between 1400 and 1500 °C is very important because the mechanical and electrical properties of stabilized zirconia based ceramics with magnesia, Mg-PSZ, are optimized for this processing¹⁸. 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, Meschke¹⁹ obtained an increasing in fracture toughness of (Mg-Y)-PSZ ceramics type, i. e., to 11.2 $\text{Mpa m}^{1/2}$ from 6.0 $\text{Mpa m}^{1/2}$ by heat treatment after sintering.

Conclusions

Precursor powders of Y₂O₃-MgO-ZrO₂ were prepared by precipitation technique. After calcination at 550 °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. $\text{m}^2 \cdot \text{g}^{-1}$. Those powders after sintering at 1500 °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-ZrO₂ crystalline phase is the main. In the sample in which Y₂O₃ was added, monoclinic phase, m-ZrO₂, was not virtually observed.

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