Journal of Materials Science and Engineering A 1 (2011) 556-561
Formerly part of Journal of Materials Science and Engineering, ISSN 1934-8959

Influence of Y_2O_3 Addition on the Microstructure and Mechanical Properties of Mg-PSZ Ceramics

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Received: April 30, 2011 / Accepted: May 12, 2011 / Published: September 10, 2011.

Abstract: Y-TZP (yttria tetragonal zirconia polycrystalline) exhibit high strength and toughness. However these ceramics degrade at low temperatures, especially when exposed to humid environments, where tetragonal to monoclinic transformation occurs because of reaction of water with tetragonal grains of Y-TZP. Mg-PSZ (magnesia partially stabilized zirconia) has better resistance to low temperatures. The addition of Y_2O_3 to Mg-PSZ is known to improve its mechanical properties by decreasing eutectoid decomposition. Mg-PSZ and Y-Mg-PSZ (yttria magnesia partially stabilized zirconia) powders were prepared by co-precipitation process. The influence of the addition of 1.7 mol% Y_2O_3 in Mg- PSZ on its microstructure and mechanical properties was investigated. Precursor powders were ground into a high energy grinder mill for 4 h, uniaxially pressed (98 Mpa) into pellets with 10 mm diameter and thickness and sintered at 1,500 °C for 1 h. Mechanical properties were evaluated by Vickers indentation technique. The microstructure has been examined by SEM (scanning electron microscopy) and the crystalline phases were analyzed by XRD (X-ray diffraction). Dense ceramics (99% of theoretical) were obtained, after sintering.

Key words: (Y-Mg)-PSZ, co-precipitation, microstructure, vickers hardness.

1. Introduction

Zirconia (ZrO_2) is a material of high technological importance and scientific interest. The intensive study of zirconia in the last decades has developed it into versatile ceramic materials. In such ceramics high temperature polymorphs of zirconia, i.e., cubic zirconia (c-ZrO_2) and tetragonal zirconia (t-ZrO_2) phases are stabilized at ambient temperature. By retention of a metastable tetragonal phase, different zirconia-toughened ceramics have been developed aiming to improve the fracture toughness of these materials [1, 2]. Addition of different stabilizing oxides, such as Y_2O_3, MgO, CeO_2 among others, is used to retain the metastable tetragonal phase. The partially stabilized zirconias (PSZ) systems of MgO-ZrO_2 [3, 4] and Y_2O_3-ZrO_2 [3-6] have both been studied extensively. Y-PSZ (yttria partially stabilized zirconia) exhibits very high strength and toughness, however it degrade at low temperature (~200 °C), particularly when exposed to a humid environment. Mg-PSZ (magnesia partially stabilized zirconia) shows much better resistance to low temperature ageing [7]. The strength of Mg-PSZ is lower than that of Y-PSZ, but its fracture toughness is much higher [8]. The microstructure of Mg-PSZ differs from Y-TZP (yttria tetragonal polycrystalline), in that the tetragonal phase is in the form of precipitates dispersed throughout a cubic matrix. In Mg-PSZ the toughening is due to the transformation of those precipitates [9]. The toughening mechanism is related to the stress-induced tetragonal to monoclinic phase transformation; as a result, high fracture toughness can be achieved in this material when containing transformable tetragonal precipitate [10]. When Y_2O_3 is added into Mg-PSZ, the t-ZrO_2 tend to stabilize, so that the process of martensitic transformation from t-ZrO_2 to m-ZrO_2 is evidently present. The ternary system ZrO_2-MgO-Y_2O_3 has mainly been studied with respect to the effect of yttria on the subeutetoid decomposition of Mg-PSZ. During ageing at

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temperatures between 1,000 °C and 1,400 °C, the cubic phase decomposes either into t-ZrO_2 (tetragonal zirconia) and MgO or into m-ZrO_2 (monoclinic zirconia) and MgO, respectively, leading to strength degradation. The addition of Y_2O_3 to the ZrO_2-MgO system suppresses this decomposition up to 1,250 °C [11]. This effect is important since it has been found that Mg-PSZ used for engine components suffers strength degradation when aged at 1,000 °C [12]. It was the object of present study to determine the effect of yttria addition on the mechanical properties and microstructure of zirconia-magnesia ceramic alloys. Addition of 1.7 mol% Y_2O_3 in Mg-PSZ was investigated.

2. Experiment

The zirconia powders used in this work were produced by coprecipitation method of the hydroxides [13]. The procedure is shown in the flow sheet of Fig. 1. The solution of cations Mg^{2+} and Y^{3+} was prepared by dissolving respectively, MgO (Merck) and Y_2O_3 (Johnson Mattey) in HCl 6M. The $ZrOCl_2$ solution was obtained from alkaline fusion of $ZrSiO_4$ Brazilian sand, process adopt at IPEN [14] (Instituto de Pesquisas Energéticas e Nucleares). The precursor solution for coprecipitation was obtained by mixing those above prepared solutions. The obtained solution was then added drop wise to a rapidly stirred NH_3 solution (pH = 10) at room temperature to obtain a coprecipitate. The coprecipitate was filtered by means of vacuum and washed with deionized water until no indication of Cl^- ions via $AgNO_3$ test. The compositions employed were 8.9 mol% MgO-91.1 mol% ZrO_2 and 1.7 mol% Y_2O_3-8.75 mol% MgO-98.3 mol% ZrO_2, denoted MZ and YMZ, respectively. The coprecipitate was then dewatered by ethyl alcohol. After dewatering, the gel (coprecipitate) was dried at 120 °C and calcined at 550 °C for 1 h. The calcined powder was ball milled for 4 h and characterized. The powder was uniaxially pressed (98 Mpa) into pellets with 10 mm diameter and thickness, which was sintered at 1,500 °C for 1 h. Densities of the sintered samples were measured by Archimed's method. Vickers hardness was measured by indentation technique [15] as well as K_{Ic}-values were calculated as follows:

$$K_{Ic} = 0.0824\ Pc^{(-3/2)} \quad (1)$$

where K_{Ic} is given in GPa $m^{1/2}$, the load P in N, the crack length c in µm.

The microstructure of sintered body o has been examined by SEM and the crystalline phases where analyzed by XRD.

3. Results and Discussion

3.1 Powders Characterization

The particle size distribution of the synthesized samples calcined at 550 °C for 1 h and grinded for 4 h, determined by QLS (Quasi Elastic Light Scattering) technique is presented in Fig. 2.

It is observed that the particle diameter size of MZ zirconia powder falls between 7 to 40 nm, the *d50 size* is ~ 18 nm. The particle diameter size of YMZ is larger than MZ particles, between 10 and 45 nm. The *d50* particle size for YMZ is ~20 nm.

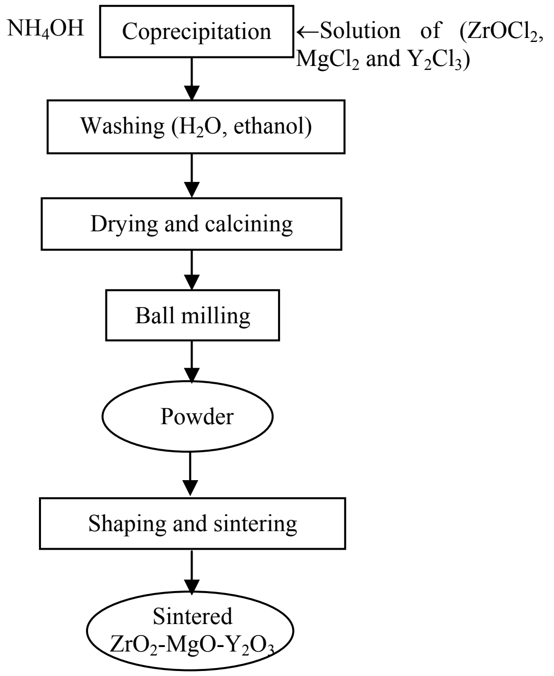


Fig. 1 Flow sheet of the experimental procedure.

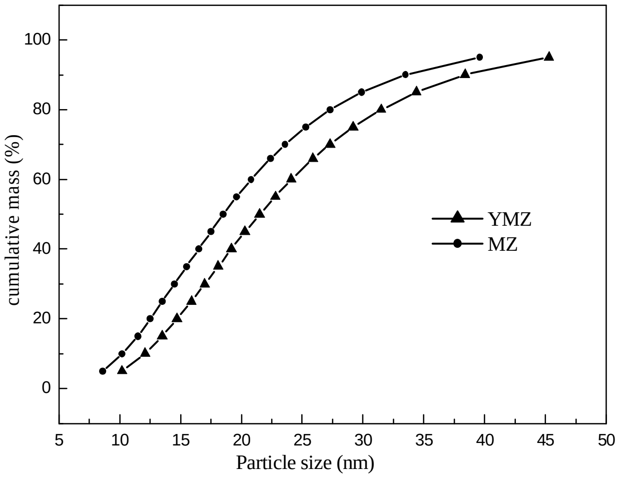


Fig. 2 Particle size distribution curve of the samples MZ and YMZ powders calcined at 550 °C for 1 h and milled for 4 h.

SEM (scanning electron microscopy) image of the sample MZ zirconia powder, in Fig. 3a, shows that the morphology of the particles is spherical like. In Fig. 3b, it is also observed the spherical particles of the sample YMZ. In the both SEM powder micrographs it can be seen particles with sub micron size, confirming the results of size distribution determined by QLS presented in Fig. 2.

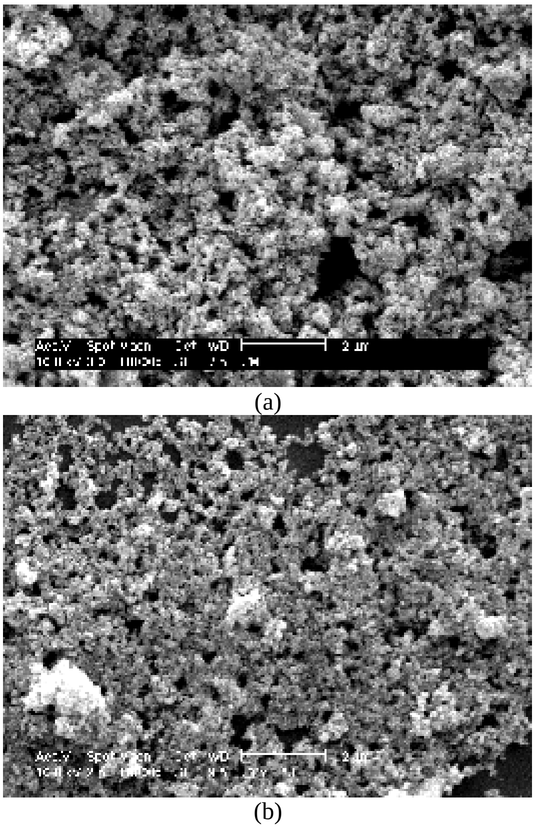
The specific surface area measured by the BET (Brunauer-Emmett-Teller) method was 64.8 $m^2 \cdot g^{-1}$ and 80.1 $m^2 \cdot g^{-1}$ respectively for MZ and YMZ. The physical characteristics of the starting powders presented above are important since strongly influence compaction behavior and densification of the powder compact [4]. Generally it is usual that the smaller the particle size of the starting powder, the greater the driving force for densification.

3.2 Microstructure and Vickers Hardness of the Mg-PSZ and Y-Mg-PSZ Ceramics

From the synthesized powders shaped into pellets by uniaxial die-pressing [16], dense ceramic were obtained after sintering at 1,500 °C, reaching 99.1% of the theoretical density, for MZ and YMZ. In Fig. 4, the XRD (X-ray diffraction) patterns of MZ, sintered at 1,500 °C for 1 h, yield the reflections of monoclinic and cubic phase. The sintered YMZ presented only the reflections of the cubic phase, as showed in Fig. 4.

The lattice parameters were calculated from Si as internal standard [17] and found to be 0.5116 nm for the MZ and 0.5114 for YMZ.

The microstructure of the samples showed significant differences. In Fig. 5a, it can see a



(a)

(b)

Fig. 3 SEM micrographs of zirconia powders: sample MZ (a) and sample YMZ (b).

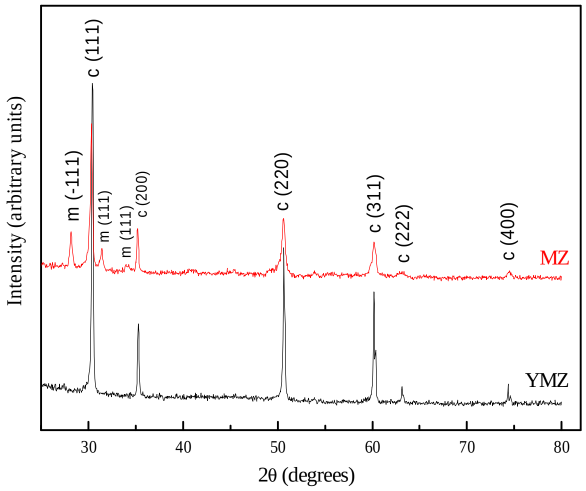
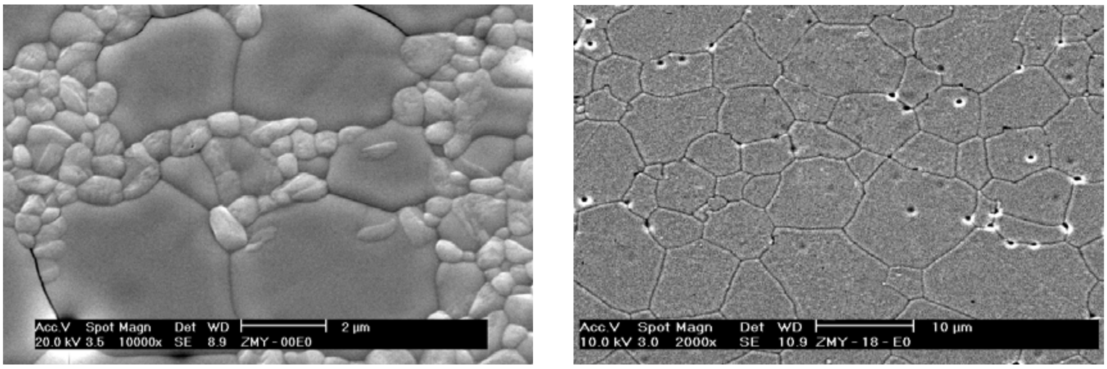


Fig. 4 XRD patterns of sample MZ and YMZ sintered for 1h at 1,500 °C.



(a) (b)

Fig. 5 SEM image of polished and thermally etched surface of MZ (a) and YMZ (b) ceramics sintered at 1500 °C for 1h.

microstructure that consists of large-grained c-ZrO_2 (cubic zirconia) and small-grained m-ZrO_2 (monoclinic zirconia) that is present at the grain boundaries of the cubic grains. In Fig 5b, it is observed that the grains are cubic morphology (polygonal grains). These observations are according to the results of XRD analysis presented in Fig. 4.

In the SEM micrograph of Fig. 6, it can be seen the fracture surface of the sample MZ. The micrograph shows transgranular cracking characteristic of c-ZrO_2, and intergranular nature of m-ZrO_2.

A typical transgranular surface fracture can be seen in SEM micrograph in Fig. 7a and this becomes in their mechanical properties. Higher magnification view of the failure site shows the polygonal grain is clear the difference of the failure characteristics between the two samples (MZ and YMZ) that certainly affect comprised of small tetragonal grains (Fig. 7b). The retention of the tetragonal grains formed within the cubic matrix [18] is of major importance since that their transformation to monoclinic phase is responsible for the high fracture toughness that Mg-PSZ exhibit [19].

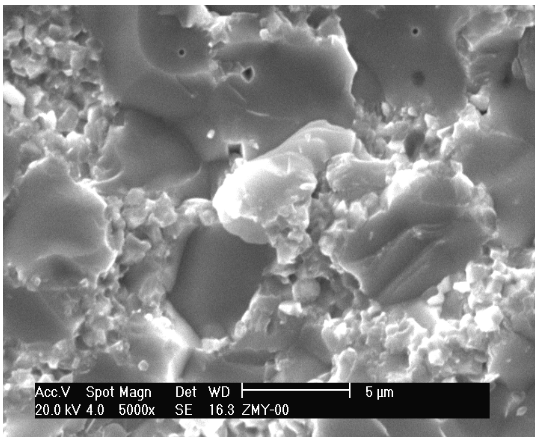


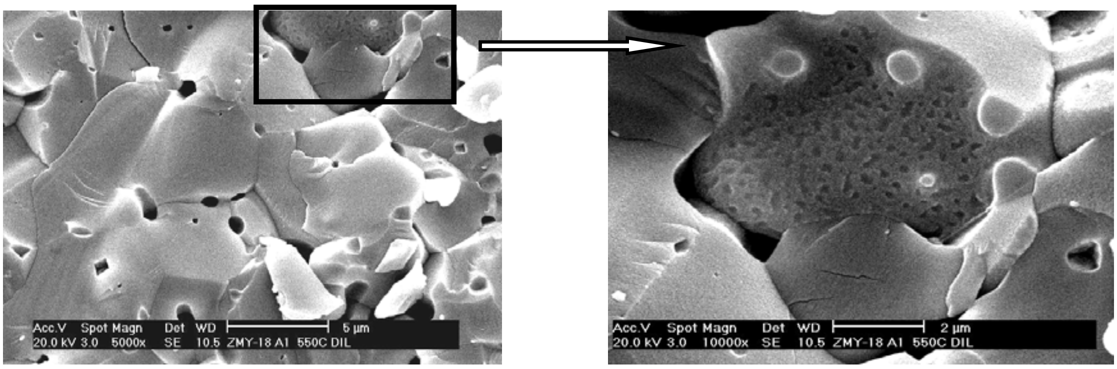
Fig. 6 SEM micrograph of the fracture surface of the sample MZ, showing transgranular (c-ZrO_2) and intergranular (m-ZrO_2) fractures.

Micro indentations were performed with loads ranging between 9.81 and 196.1 N to produce cracking at the corners of the indentation imprint, so that the mechanical properties could be evaluated. The mechanical characteristics of MZ and YMZ are listed in Table 1.

Comparing the results of two zirconias, the Vickers hardness was slight high for the second sample (YMZ), Y_2O_3 was added. The Vickers harnesses and K_{IC} values obtained in this study are comparable to the published values [11, 19-22].

4. Conclusions

Fine grained Mg-ZrO_2 (Mg doped zirconia) and Y-Mg-ZrO_2 (Y-Mg doped zirconia) powders composites have been synthesized by coprecipitation method. The addition of Y_2O_3 in the MgO-ZrO_2 system plays an important role in the microstructural and subsequent mechanical properties upon sintering. In sintered Mg-ZrO_2, cubic and monoclinic phases are present. The addition of Y_2O_3 yields relatively coarse-grained microstructure; the grains are predominantly cubic morphology with fine precipitates of tetragonal phase. Mg-ZrO_2 ceramic showed transgranular and intergranular fracture characteristics



(a) (b)

Fig. 7 SEM micrograph of the fracture surface of the sample YMZ showing transgranular (c-ZrO_2) crack (a) and small tetragonal grains formed within the cubic matrix (b).

Table 1 Mechanical properties of Mg doped zirconia (MZ) and Y-Mg doped zirconia (YMZ) sintered at 1,500 °C for 1 h.

Sample	Composition (mol%)	Vickers hardness H_v (GPa)	K_{IC} ($MPa \cdot m^{1/2}$)
MZ	8.9 (MgO) - 91.1(ZrO_2)	10.90 ± 0.32	6.63 ± 0.51
YMZ	1.7 Y_2O_3 - 8.75 MgO - 89.55 ZrO_2	14.80 ± 0.84	5.30 ± 0.18

whereas in Y-Mg-ZrO_2 only the transgranular cracking was observed. Mg-ZrO_2 with the composition 8.9 mol% MgO and 91.1 mol% ZrO_2 presented H_v (Vickers hardness) of 10.90 GPa and K_{IC} of 6.63 $MPa \cdot m^{1/2}$. Y-Mg-ZrO_2 with the composition 1.7 mol % Y_2O_3, 8.75 mol% MgO and 89.55 mol% ZrO_2 showed H_v of 14.80 GPa and K_{IC} of 5.3 $MPa \cdot m^{1/2}$.

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