Characteristics of $MgO-Y_2O_3-ZrO_2$ Powders Prepared by Coprecipitation Method From different Starting Solutions

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Abstracts
$MgO-Y_2O_3-ZrO_2$ was prepared by coprecipitation of hydroxides, using different starting solutions: zirconium oxychloride and zirconyl nitrate. NH_4OH solution was used as precipitant. The obtained powders were characterized by TGA (thermal gravimetric analysis) and DTA (differential thermal analysis), BET technique, XRD (X-ray diffraction analysis) and SEM (scaning electronic microscopy). The starting solutions greatly influence the characteristics of the resulting precipitates, which resulted in different microstructure after sintering. The coprecipitation from diluted metal solutions resulted in highly hard agglomerated powders whereas concentrated solutions yielded a soft and finely divide powders. The tetragonal and cubic zirconia was stabilized after sintering the powders at 1500^0C for 1h and bulk densities were >95% of theoretical.

Introduction

Pure zirconia has three polymorphic forms: monoclinic (m), tetragonal (t), and cubic (c). At room temperature, zirconia is monoclinic, which changes to tetragonal above 1170°C and to cubic above 2300°C. The martensitic nonoclinic to tetragonal phase transformation contributes to the toughening of zirconia ceramics [1]. During the last decade, various ZrO_2-based ceramics have been developed. In these ceramics, tetragonal and cubic phases (high temperatures polymorphs) can be achieved at room temperature by adding stabilizers such as MgO, CaO, Y_2O_3 and CeO_2. Magnesia partially stabilized zirconia (Mg-PSZ) [2,3] has been used for a wide range of applications such as lining segments for pumps, ball bearings, pistons, guide rollers for wire productions etc. An inherent problem in Mg-PSZ binary system is decomposition of tetragonal and cubic to monoclinic zirconia and magnesia at high temperatures [4]. For example when Mg-PSZ is used as shaping tools it suffer frequent high temperature heating, where phase stability becomes an issue. In extrusion die applications, the material has to resist high temperature and pressure, and consequently problems of hydrothermal stability arise. The ternary system $MgO-Y_2O_3-ZrO_2$ has been object of studies with respect to effect of Y_2O_3 on the subeutectoid decomposition of Mg-PSZ [5]. The addition of Y_2O_3 to MgO-PSZ binary system was found to significantly inhibit the kinetics of decomposition of cubic phase [6,7]. Moreover, the fabrication process parameters should be such that both size and distribution of zirconia particles should be very small and these particles are homogeneously distributed in matrix material. Therefore, preparation of optimum quality powder is extremely important for achieve those ceramics. It is also important to determine the factor that stabilizes the metastable phases (t and c zirconia) against the stable one (m zirconia) at relatively low temperatures, especially when preparation methods of precipitation are employed for the precursor material. Several methods of ZrO_2 precursor preparation have been reported in the literature. By chemical methods, in which zirconium hydroxide is a key precursor, frequently a fine, homogeneous and high sinterability powders is reached. In those methods the final characteristics and properties of the powder are affected by preparation conditions. For example Torralvo [8] and Zaitsev [9] have varied starting zirconium salt solution to obtain the

zirconium hydroxide. Benedetti [10] obtained ultra-fine zirconia powders by precipitation from $ZrOCl_2$ using either NaOH and NH_4OH. The effect of pH of precipitations has been investigated by Davis [11] and Srinivasan [12] has verified the effect of varying the rate of base addition on zirconium hydroxide characteristics. Readey [13] obtained soft agglomerated powders by precipitates washing with alcohol. The object of this work is to prepare ZrO_2-MgO-Y_2O_3 powders by coprecipitation, from zirconium oxichloride and zirconyl nitrate and their characterization. The concentration of start solutions was varied to verify its effects on characteristics of final zirconia powders. Samples obtained from both start solutions were sintered for microstructure observations.

Experimental

Zirconyl chloride and zirconyl nitrate solutions were prepared by dissolution of zirconium hydroxide (derived from basic sulfate precipitation method [14] in hydrochloric and nitric acid respectively. These solutions were used as starting materials. Y_2O_3 (99,99% purity, John Mattey, Alpha Products) and MgO (Analytical Grade) were dissolved in above prepared solutions in quantities to obtain 8,75% mol MgO and 1,6% mol Y_2O_3 in final oxide composition. A gel of zirconia (hydrated zirconium) with desired composition was precipitated from chloride and nitric solutions, using NH_4OH solution, according to following procedure. The starting solution (zirconyl chloride or zirconyl nitrate solution) was added into a volume previously calculated of 3N NH_4OH, to obtain pH 10 at the end of the precipitation. The addition was performed at a rate of 4mL/min, from a burette, while the NH_4OH solution was mechanically stirred. The precipitate of (MgO-Y_2O_3) ZrO2 gel was filtered and repeatedly washed with distilled water to remove chloride (nitrate) ion. The precipitate was aged in ethanol for 3h at 50°C to minimize hard agglomerates, followed by vacuum filtration and dried in a oven at 70°C for 24 h and calcined at 800°C for 1 h. The dried precipitate was evaluated in terms of weight loss by TGA; simultaneously differential thermal analysis (DTA) was performed at heating rate of 10°C/min up to 800°C. The BET method (nitrogen adsorption) was used for specific surface area determination, laser method for determination of agglomerate size and scanning electron microscopy (SEM) for microstructure observations. Considering in favor of sinterability, two calcined samples were chosen to sintering. The calcined powders were uniaxially pressed into pellets at 150 Mpa and were sintered in air at 1500°C for 1 h. Bulk densities were determined by Archimedes method and the microstructure was observed by SEM.

Results and Discussion

The conditions of coprecipitation are present in Tab 1.

Table 1-Conditions of samples coprecipitation, using 3N NH_4OH as precipitant

Sample*	Concentration of Metals Starting Solution (Mol/L)	Medium
YZM-N05	0.5	Zirconyl nitrate
YZM-N12	1.2	
YZM-C05	0.5	Zirconyl chloride
YZM-C12	1.2	

*Composition of all samples were 8,75% mol MgO and 1,6% mol Y_2O_3 in final oxide, considering the reasons presented in previous work [15]

The gelatinous precipitate obtained from diluted solution of metals (YZM-C05 and YZM-N05) after dried at 70°C they shrank and formed a hard cake with glassy appearance. These materials are difficult to handle, but when they was placed in ethanol, small particles of about some mm size were obtained, which were more easily handled. By crushing in a mortar with pestle and drying again at 70°C, fine sand like product was yield. When the precipitation was performed with concentrate metals solution (YZM-C12 and YZM-N12), the gels obtained, after drying at 70°C, opaque and soft lumps resulted. Those soft products were easily crushed in a mortar, without any solvent and finely divided powders were afforded. The characteristics of crushed powders calcined at 600^0 C for 1h are shown in Tab 2.

Table 2-Characteristics of crushed powders calcined at 600^0 C

Sample	Specific Surface Area (m^2/g)	Average Agglomerate Size (μm)
YZM-N05	56	23.94
YZM-N12	70	2.97
YZM-C05	55	6.13
YZM-C12	65	1.03

It can be observed that samples precipitated from nitric medium (YZM-N05 and YZM-N12) presented higher specific surface area than those obtained from chloride medium (YZM-C05 and YZM-C12). In both medium, high concentration of metals yielded high surface area and low concentration, low surface area. Small average agglomerate size was reached from high concentration of metals and larger particles were obtained from low concentration. The sample YZM-N05 presented a high average agglomerate size (23,94μm) than that of sample YZM-C05 (6,13 μm), even both samples having practically the same specific surface area (56 and 55 m^2/g respectively), indicating that the first one is porous nature. The particle size distribution of the crushed powders calcined at 600^0Cfor 1h is shown in Fig. 1.

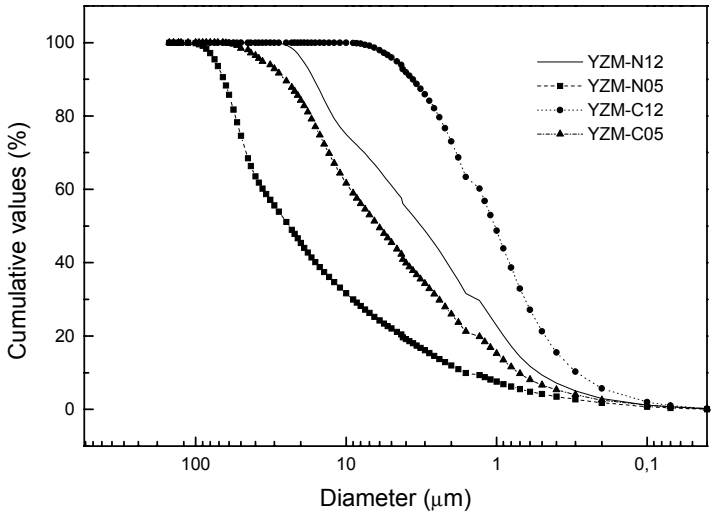

Fig.1-Particle size distribution of crushed powders calcined at 600^0C for h.

It can be seen 50% of the particles size are below 10 μm except for sample YZM-N05. Fig 2 shows SEM micrographs of these powders. In Fig 2a (YZM-C05) and 2b (YZM-N05) it can be observed the

hard characteristic of the materials and it can notice that the size of agglomerates agrees with the results shown in Table 2. Fig 2c (YZM-C12) and 2d (YZM-N12) show that the agglomerates are soft like and the particles are sub micrometric dimensions.

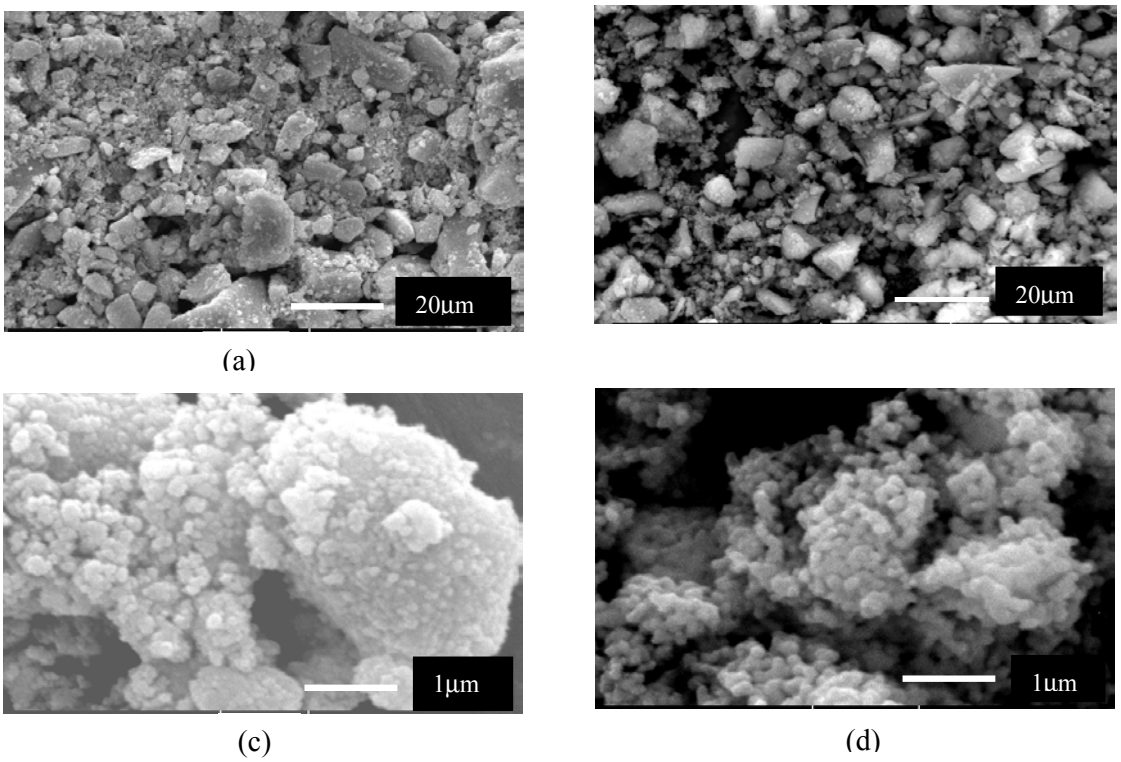

Fig.2-Micrographs of samples YZM-C05 (a) , YZM-N05 (b), YZM-C12 (c) and YZM-N12 (d) calcined at 550^0C

The samples YZM-C12 and YZM-N-12 were chosen for sintering, considering characteristics in favor of sintering, small average particle size and high specific surface area. Fig 3 shows the DTA (a) and TGA (b) curves of these samples after dried at 70^0C for 24h.

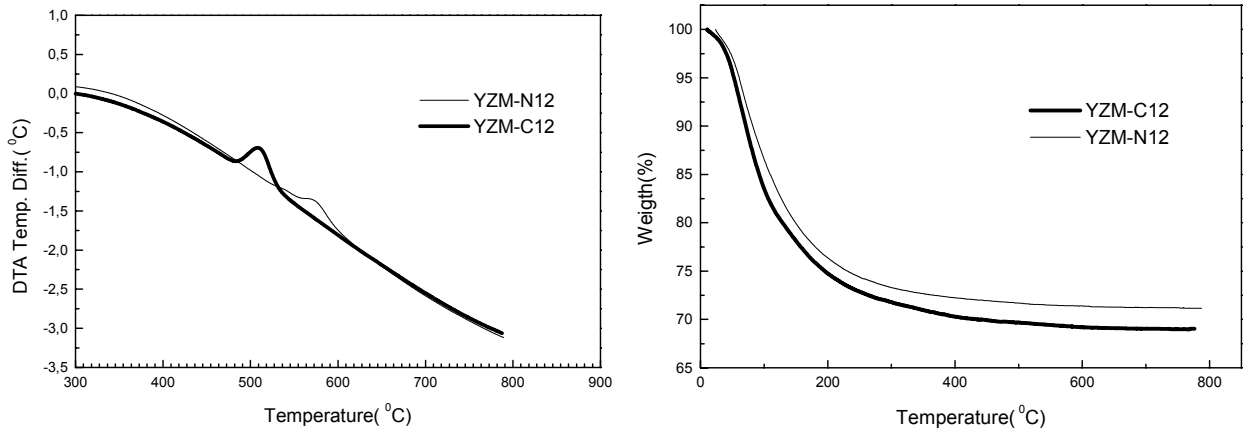

Fig.3- DTA (a) curve at hating rate of 10^0C/min in air, from 300^0C to800^0C and TGA (b) curve at the same conditions, from room temperature to 800^0C, of samples after drying at 70^0C for 24h.