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MICROWAVE–HYDROTHERMAL TREATMENT OF MECHANICAL MIXTURES OF ZrO_2 XEROGEL AND CRYSTALLINE Y_2O_3

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Mechanical mixtures containing zirconia xerogel and increasing amount of crystalline yttria up to 40 mol%, were hydrothermally treated by microwave route at 110°C for 2 h. All the treatments were performed in the presence of $(KOH+K_2CO_3)$ mineralizer solution at concentration 0.2 M.

Amorphous and hydrated $ZrO_2–Y_2O_3$ solid solutions with yttria content up to 33.3 mol% (corresponding to Zr/Y molar ratio equal to 1), resulted after the hydrothermal treatments.

A remarkable reduction of the surface area has been detected at increasing yttria content of the amorphous phases with a corresponding increase of the exothermic peak of crystallization.

A mechanism of reaction for the formation of the amorphous solid solutions has been proposed.

Keywords: *amorphous hydrated zirconia–yttria solid solutions, crystallization temperature, microwave–hydrothermal treatment, surface area*

Introduction

The use of amorphous co-precipitates as precursors for the production of advanced ceramics, is of special interest for several high-performance applications. Co-precipitates based on $ZrO_2–Y_2O_3$ system have attracted much attention in different fields [1–3]. In spite of the high purity and homogeneity of these precursors, their high reactivity determines a fast coarsening of the primary particles when they are heated at high temperatures and, consequently, hard aggregates result. In this circumstance a preliminary milling is necessary for the subsequent process of densification. To avoid the milling step, a hydrothermal treatment is suggested which allows to obtain powdered precursors characterized by low degree of agglomeration, soft and mouldable.

The hydrothermal treatments are generally performed in a rather high range of temperatures, so making complex and expensive the process with obvious difficulties to reproduce it industrially [4–7]. A less expensive and simple hydrothermal treatment performed at the boiling temperature of the starting suspension, furnished zirconia-based powders characterized by a poor crystallinity [8], so they were not very different from the amorphous precursors. Nanometric yttria-stabilized zirconia powders characterized by relatively high crystallinity, low degree of agglomeration, soft and mouldable, were synthesized from mechanical mixtures of zirconia xerogel and crystalline yttria at temperature close to the boiling temperature [9–12]. Such precursors showed high performances when they were directly sintered [13]. However, reaction times of hydrothermal treatment still (72 h) long were required for the full crystallization.

In order to reduce the reaction times and to ascertain the crystallization–stabilization of mechanical mixtures of zirconia xerogel and crystalline yttria, the microwave–hydrothermal method has been adopted. It is well-known that the microwave route allows to reduce both reaction times and the temperature of the treatment [14]. All the treatments have been performed in the presence of diluted solution (0.2 M of (K_2CO_3+KOH) mineralizer).

Experimental

A stock of zirconia xerogel was prepared by adding $ZrCl_4$ solution to ammonia (~4 M) as precipitating agent under continuous stirring. The precipitate was washed repeatedly with distilled water for complete removal of Cl^-, then washed with ethanol, and finally dried at 60°C. Several fractions of the stock were taken and mixed with different amount of crystalline Y_2O_3 in agate mortar, in the presence of acetone. Each resulting mixture was added to a diluted (0.10 M) solution of (K_2CO_3+KOH) mineralizer having the K_2CO_3/KOH molar ratio constant and equal to 3. The adopted solid/liquid mass ratio was also constant and equal to

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1/40. Each microwave–hydrothermal treatment was carried out at 110°C for a reaction time of 2 h. After the treatments, the resulting products were washed several times with distilled water to remove the excess of the mineralizer and dried in air at 60°C for 24 h.

X-ray diffraction analyses (XRD) were performed using a diffractometer X'PERT of Philips and the CuK_α radiation. The products were also characterized by simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TG) (Netzsch thermoanalyzer, mod. STA 409), with α-Al_2O_3 as a reference and a 10 K min^{-1} heating rate. The simultaneous DTA and TG were also performed with an intermediate step consisting in an isothermal treatment at 100°C for 45 min.

The specific surface areas of the powders were determined by the BET method using a Gemini instrument from Micromeritics and utilizing nitrogen as the adsorbate after drying at 60°C.

The microstructure of the powders were revealed with scanning electron microscopy (SEM) whereas the elemental analysis was contemporaneously done by using EDAX.

Results and discussion

Figure 1 shows the XRD powder patterns of the products synthesized from the mechanical mixtures of zirconia xerogel with increasing amount of crystalline yttria. With the exception of the mixture richest in the yttria content, single amorphous products result after the treatment of each mixture at 110°C for 2 h in the presence of 0.2 M solution of the mineralizer. The changes in the wide angle X-ray scattering patterns presented in function of the mole yttria fraction indicate that the characteristic Bragg reflections of the crystalline yttria appear over the 1:1 Y/Zr stoichiometric ratio. It is supposable that the transformation of crystalline Y_2O_3 into the amorphous state is to be related to its reaction with the very reactive zirconia xerogel. In fact, a small fraction of un-reacted crystalline yttria has been detected only for the mixture with mole fraction of $YO_{1.5}$ equal to 0.57. Supposing an isomorphic substitution of Zr for Y, amorphous and hydrated solid solutions must be considered as it was assumed for zirconia–yttria co-precipitates with less content of Y_2O_3 [3].

The remarkable reduction in the surface area from 310 to 50 m^2 g^{-1} of the products at the increasing mole fraction of $YO_{1.5}$ (Fig. 2), demonstrates the effective reaction between the zirconia xerogel and the crystalline yttria. A further and direct demonstration of the reaction with formation of amorphous solid solutions is given in Fig. 3, which reports SEM–EDAX analyses of

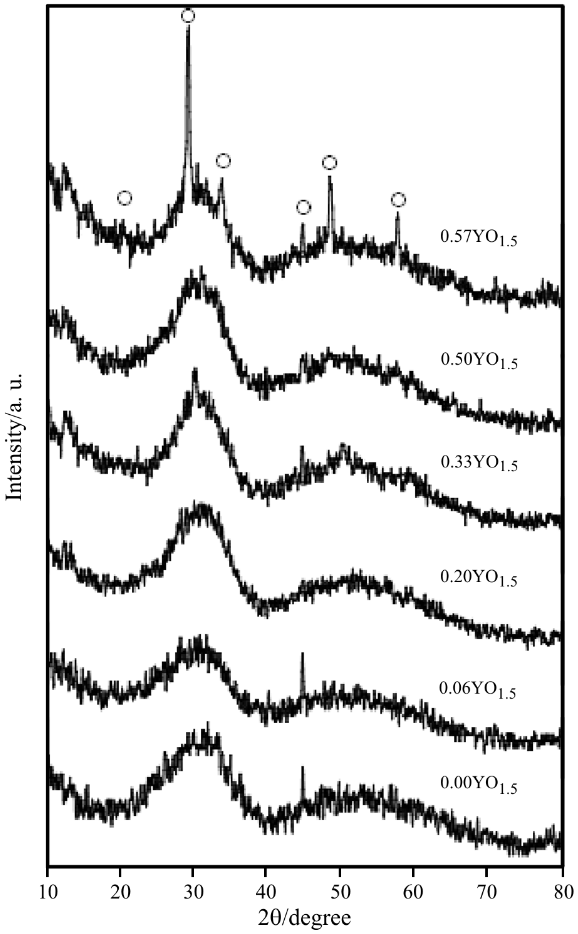

Fig. 1 XRD powder patterns of the products microwave-hydrothermally synthesized at 110°C for 2 h from the mechanical mixtures of zirconia xerogel and crystalline Y_2O_3 with increasing amount of yttria (o – crystalline Y_2O_3)

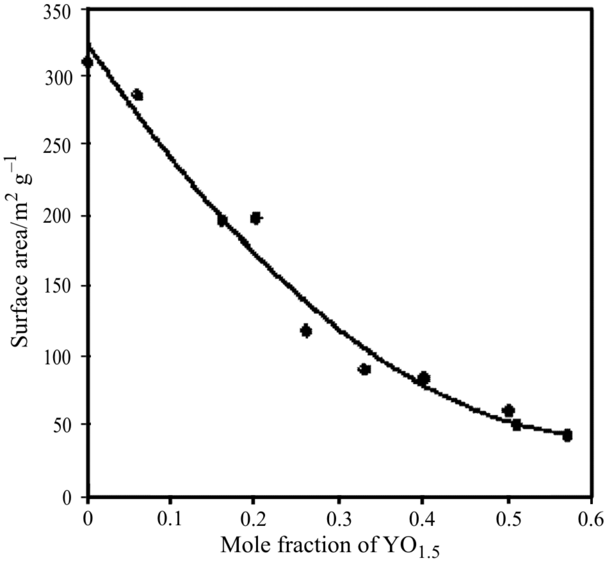

Fig. 2 Surface area of the synthesized powders listed in Fig. 1 as a function of the mole fraction of $YO_{1.5}$

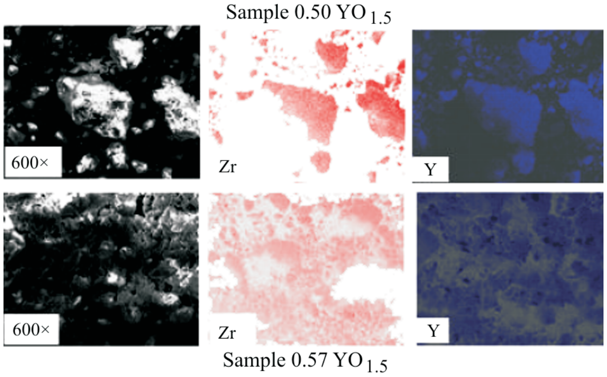

Fig. 3 SEM-EDAX analyses of synthesized products with mole fraction of $YO_{1.5}$ equal to 0.50 and 0.57, respectively with the presence or not of free crystalline Y_2O_3

two products with mole fraction of $YO_{1.5}$ equal to 0.50 and 0.57, respectively. The product poorer in the yttria content does not contain free crystalline Y_2O_3, whereas the one with $YO_{1.5}$ equal to 0.57 contains a certain fraction of un-reacted crystalline Y_2O_3. The locations of both Y and Zr ions are the same in the case of $0.50YO_{1.5}$, while those differ at $0.50YO_{1.5}$. Moreover, there are spots with high contrast of yttria clearly showing the heterodispersive distribution of the un-reacted Y_2O_3 grains. Such findings allow to declare that amorphous and hydrated zirconia–yttria solid solutions are obtained from the mechanical mixtures and that the maximum solubility of yttria corresponds to a mole fraction of $YO_{1.5}$ equal to 0.5.

It is well known that amorphous ZrO_2 xerogel precipitated with ammonia, shows in DTA a sharp exothermic peak of crystallization into metastable tetragonal ZrO_2 at 420°C [15], whereas a (Y–Zr) hydroxide co-precipitate xerogel (8 mol% Y_2O_3) shows an analogous and sharp exothermic peak at 445°C due to the crystallization of zirconia in the cubic polymorph [9]. The typical DTA curves of two of the synthesized products and characterized by a mole fraction of $YO_{1.5}$ equal to 0.16 and 0.50, respectively, are shown in Fig. 4. It is confirmed that the crystallization temperature is a function of the yttria content of the amorphous phases, in particular higher the yttria content, higher the crystallization temperature as results in Fig. 5 for all the synthesized products. The crystallization temperature changes, in fact, from 425°C for the hydrothermally treated and undoped zirconia xerogel up to 475°C for the synthesized products richer in the yttria content. An approximate linear correlation results by plotting the crystallization temperature as a function of the surface area of the products (Fig. 6). In fact, higher the surface area, lower the crystallization temperature of the corresponding product results.

Figure 7 shows the TG curves of the two same products listed in Fig. 4. The analyses have been per-

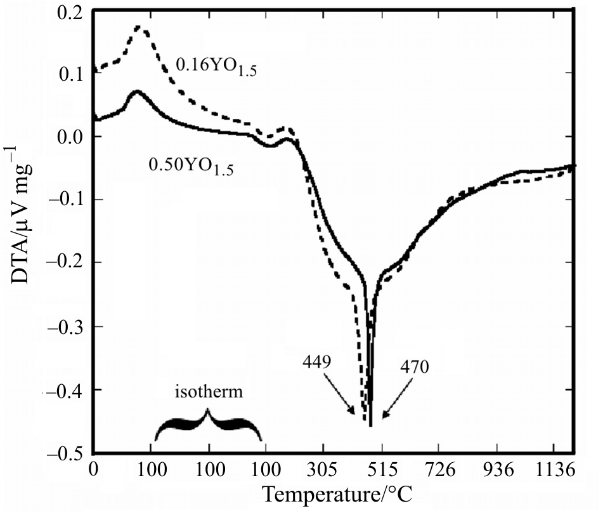

Fig. 4 DTA curves of two products with different yttria content

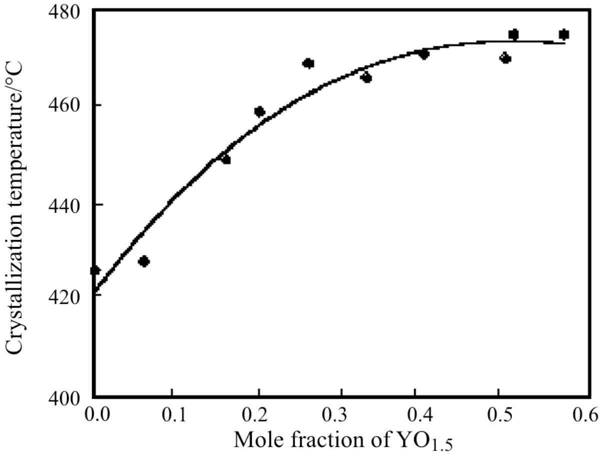

Fig. 5 Crystallization temperature of products as a function of the yttria content

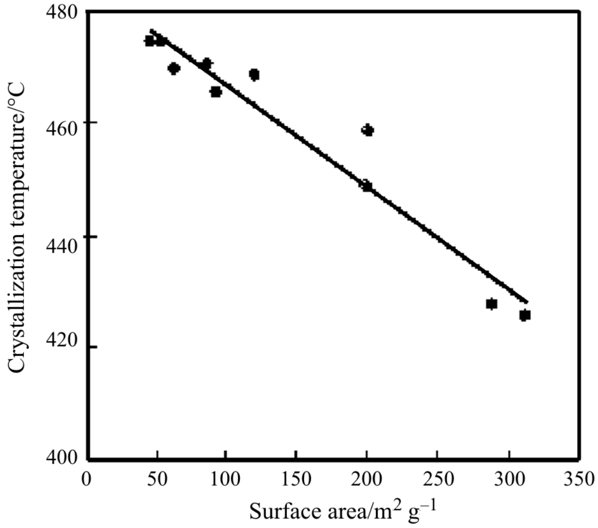

Fig. 6 Crystallization temperature as a function of the surface area of the products

formed with an intermediate isotherm at 100°C for 45 min. After the isotherm, a lower mass loss results for the sample richer in yttria content, whereas a higher mass loss has been detected for the product poorer in yttria content. Comparable mass losses result for all the products at temperature higher than 100°C. In this case, such losses take place at relatively higher temperature for the products with increasing yttria content. The mass loss can be mainly attributed to the loss of H_2O moles of the constituting OH^-, H^+, H_2O species of the products. Considering the general formula of the products as $Zr_{(1-x)}Y_xO_{(2-x/2)}\cdot yH_2O$ with $0 \leq x \leq 0.5$, the loss of H_2O moles per unit formula (y) has been calculated both after the isotherm at 100°C and in the correspondence of the temperature range between 100 and 1200°C. The results are summarized in Fig. 8 which shows the loss of H_2O moles after the isotherm (Fig. 8a), the loss at higher temperature (Fig. 8b), and finally the total loss (Fig. 8c) as a function of the yttria content of the products. At increasing yttria content, a progressive reduction of both the loss of H_2O moles after the isotherm and the total loss can be observed, whereas a slightly increase of the loss results at higher temperature. Such behaviour has been related to the progressive reduction of the content of the constituting H_2O moles with a corresponding increase of the constituting OH groups at increasing yttria content of the products.

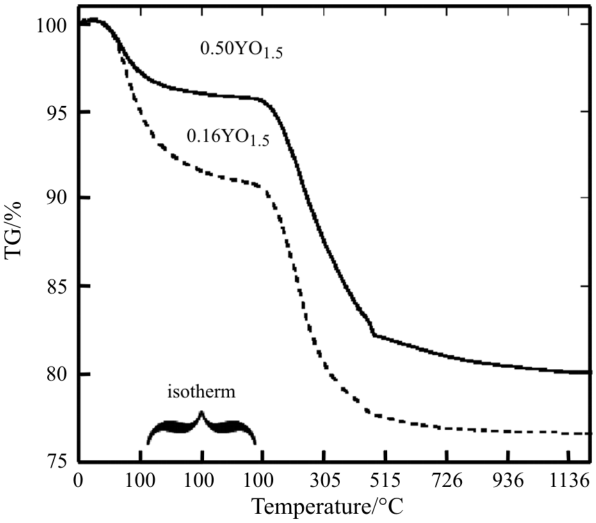

Fig. 7 TG curves of the products listed in Fig. 4 showing the mass loss after the isotherm at 100°C and the corresponding mass loss after the isotherm

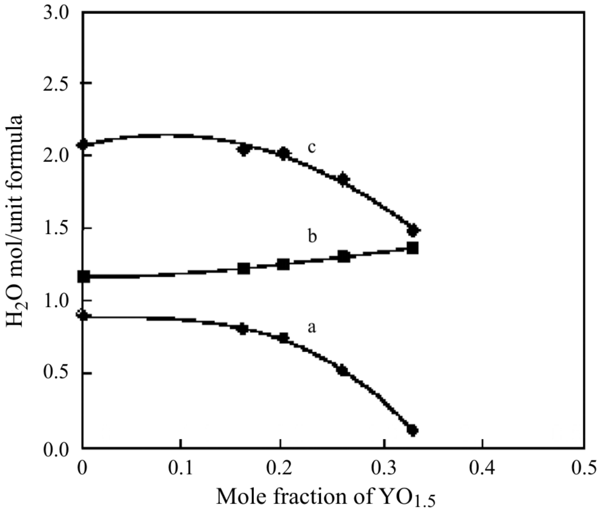

Fig. 8 Loss of H_2O mol/unit formula of products as a function of the yttria content; a – mass loss of the H_2O moles after the isotherm, b – loss of the H_2O moles between 100 and 1200°C and c – total loss of H_2O moles

Conclusions

A microwave–hydrothermal treatment for 2 h at the boiling temperature of the diluted solution of the mineralizer containing the mechanical mixtures of zirconia xerogel and crystalline Y_2O_3, is insufficient for the crystallization of yttria-doped zirconia. The treatment determines the formation of amorphous and hydrated zirconia–yttria solid solutions according to the reaction:

$$\begin{gathered}\mathrm{ZrO_2}\ \text{(xerogel)}+\mathrm{Y_2O_3}\ \text{(crystalline)}\rightarrow\\ \text{hydroxide hydrated of Zr and Y (amorphous)}\end{gathered}$$

This step is equivalent to the zirconia–yttria coprecipitation from aqueous solutions containing both Zr and Y, respectively.

At increasing yttria content in the products, a progressive reduction of the constituting H_2O moles with a corresponding slightly increase of the constituting hydroxide groups, characterized by a relatively higher thermal stability, has been detected.

As surface area, hydration state and defects concentration affect the ion surface mobility, the synthesized products appear of interest in ion transport properties.

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