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Journal of the European Ceramic Society 25 (2005) 2017–2021

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Films by slurry coating of nanometric YSZ (8 mol% Y_2O_3) powders synthesized by low-temperature hydrothermal treatment

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Available online 14 April 2005

Abstract

Nanocrystalline powders of yttria (8 mol.%)-stabilized zirconia have been hydrothermally synthesized from mechanical mixture of ZrO_2 xerogel and crystalline Y_2O_3 by conventional or microwave route, respectively. The treatments have been performed at 110 and/or 150 °C for 2 h up to 72 h, and in the presence of diluted (0.2 M) or concentrated solution (2.0 M) of ($KOH + K_2CO_3$) mineralizer.

To reduce the degree of agglomeration, the freshly synthesized powders has been treated under stirring with aqueous solution of poly(vinyl alcohol) (PVA 10 wt.%) for 15 h at pH 6.8, whereas to favour the formation of coating suspensions, the polymer absorbed powders and poly(ethylene glycol) (PEG) have been added to ethanol/water solution and stirred under ultrasonic agitation.

With the different suspensions, various films have been deposited on glass substrates through withdrawal-coating. After drying at 60 °C and firing at 600 °C, the texture of the different films has been examined and compared with analogous films deposited by the sol–gel method.

The effects of both the type of hydrothermal treatment, the concentration of the mineralizer, and the withdrawal-coating speed on the texture of the films are discussed.

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Keywords: Films; Porosity; Ionic conductivity; ZrO_2–Y_2O_3; Fuel cells

1. Introduction

Yttria (8 mol.%)-stabilized zirconia (8Y-SZ) is a remarkable material due to its high performances in terms of oxygen–ion conductivity, thermal and chemical stability. At present, 8Y-SZ films are of growing interest for their applications in electrochemical devices.[1] Hence, several preparation techniques based on reactive sputter deposition,[2–4] sol–gel,[5,6] chemical vapour deposition (CVD)[7] and deposition of weakly agglomerated nanometer-particles dispersion (slurry coating),[8,9] have been investigated to prepare Y-SZ films on different substrates.

The preparation of films by slurry coating technique allows a good control of the thickness,[9] a reduction of the sintering temperature especially when nanometer-sized dispersions are used, and finally a reduced crystal growth which favours a fine texture of the film.[10]

For the deposition of homogeneous films by slurry coating technique, it is essential to dispose of a suspension with a high dispersion of the particles, high stability against the flocculation, nanometer-sized and weakly-agglomerated primary particles, and finally a high concentration of the particles.

In order to obtain highly homogeneous and nanometer-sized powders of yttria-stabilized zirconia, several methods of synthesis have been proposed.[11–18] Most syntheses are based on solution chemistry methods. However, the nanometer-sized primary particles and the homogeneity of the powders do not ensure the stability against the flocculation of the corresponding suspension; it is also essential to dispose of weakly-agglomerated primary particles. Syntheses by polymerisation routes[11,16] favour the formation of non-agglomerated and nanometer-sized YSZ powders, however, the thermal decomposition of the massive organic component might affect the texture of the growing film.

To improve the stability of suspension against the flocculation, the polymeric adsorption onto the surface of the powders appears as an effective method. Various polymers have

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doi:10.1016/j.jeurceramsoc.2005.03.006

been tested for polymer-adsorption on the surface of metal oxides in aqueous suspensions.[9,19] Uniform and porous thick films of Y-SZ were deposited on dense α-Al_2O_3 substrates by Zhang et al.[8] To favour the dispersion of the nanoparticles in the aqueous suspension, an adsorption of poly(vinyl alcohol) (PVA) was performed, whereas poly(ethylene glycol) (PEG) was selected as the reagent assisting the film formation. The saturated amounts of the adsorbed PVA and PEG were 0.74 and 0.2 mg/m^2, respectively. Being the BET surface area of untreated Y-SZ powder of 145 m^2/g, an organic component higher than 10% by weight must expected and, consequently, a percent by volume still higher so determining the formation of porous film.

In a recent paper,[20] 8Y-SZ powders, characterized by low degree of agglomeration, have been synthesized from mechanical mixture of zirconia xerogel and crystalline yttria in the presence of diluted solution (0.2 M) of ($KOH + K_2CO_3$) mineralizer.

The aims of the present paper concern 8Y-SZ powders synthesizable in the presence of dilute (0.2 M) or concentrated (2.0 M) solutions of the mineralizer, and adopting conventional (CHT) or microwave-hydrothermal (MHT) treatments at 110–150 °C. The resulting powders will be treated with PVA as a dispersant and PEG assisting the film formation. The various suspensions will be deposited on glass substrates for the preparation of films in order to investigate the effects of different parameters on the quality of the films. As a comparison, the corresponding films by the sol–gel technique will be also investigated.

2. Experimental

A stock of a mechanical mixture containing zirconia xerogel and crystalline yttria was prepared according to a previous paper.[20] The hydrothermal treatments were performed in the presence of dilute (0.1 M) or concentrated (2.0 M) solution of ($KOH + K_2CO_3$) mineralizer, and taking the KOH/K_2CO_3 molar ratio constant and equal to 1/3. The reaction time and the temperature of the CHT, were 72 h and 110 °C, respectively, whereas the MHT were performed in two steps: the first one at 110 °C for 1 h followed by a second step at 150 °C for 2 h. After the hydrothermal treatments the products were washed several times with distilled water until to remove the mineralizer. A fraction of each product was dried at 60 °C and characterized by XRD, simultaneous DTA-TGA, the average crystal sizes were calculated by the Scherrer formula, and finally the BET surface area was determined utilizing nitrogen as the adsorbate after drying the powders at 60 °C.

The remaining fraction of each freshly product was treated under continuous stirring with an aqueous solution (7 g/L) of PVA (10 wt.% of PVA in respect to the mass of the synthesized powder) for 15 h adjusting the pH of the suspension at 6.8. Several washings were performed with distilled water to remove the excess of PVA. The infrared spectra were obtained with a FTIR spectrometer in the 400–4000 cm^{-1}. The polymer-adsorbed powder and PEG (5 wt.% of PEG in respect to the mass of the synthesized powder) were added to ethanol/water solution (20 g/L) and stirred for 30 min under ultrasonic agitation. The resulting suspensions were employed in the preparation of the films.

Zirconium propoxide, $Zr(OC_3H_7)_4$ (70 wt.% in 1-propanol; Aldrich) and yttrium chloride hexaydrate, $YCl_3\cdot 6H_2O$ (99.9%, Acros), were used as starting materials in the sol–gel preparation. Alcoholic solutions of zirconium propoxide were prepared at room temperature using anhydrous ethanol. Acetylacetone (Acyac) was also added to control the hydrolytic activity of zirconium alkoxide. The molar ratios employed were: $Zr(OC_3H_7)_4$:EtOH:Acyac:H_2O = 1:24:0.7:3. In order to obtain a nominal composition corresponding to 8Y-SZ, a stoichiometric amount of $YCl_3\cdot 6H_2O$ was then added to the solution under continuous stirring.

Carefully cleaned glass substrates were dipped into the various suspensions or in the sol solution and withdrawn at a speed of 200 and 400 mm/min, respectively. The supported films were firstly dried at 60 °C and then thermally treated at 600 °C for 3 h. The morphology of the films were observed by scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows the XRD powder patterns of the starting mechanical mixture of ZrO_2 xerogel in mixture with

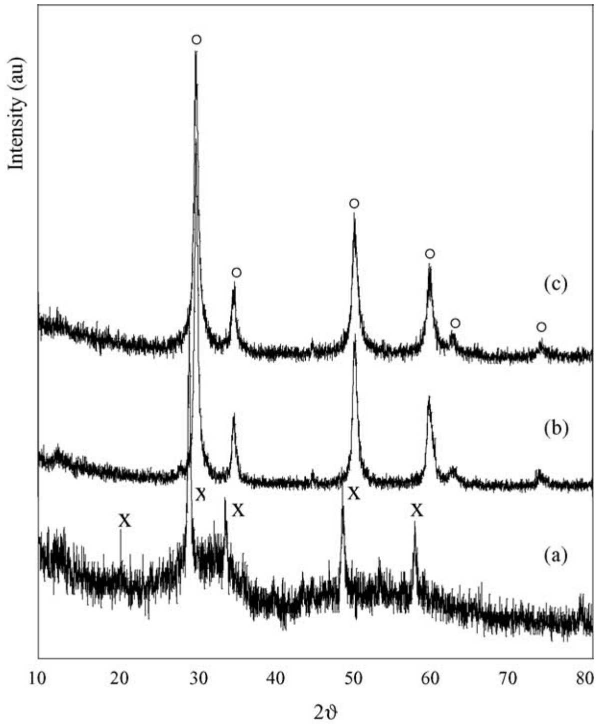

Fig. 1. XRD powder patterns of the mechanical mixture of ZrO_2 xerogel and crystalline Y_2O_3 (a); and of the corresponding products synthesized by CHT at 110 °C for 72 h in the presence of dilute (0.2 M) (b) or concentrated (2.0 M) solution (c) of the mineralizer (○, c-ZrO_2; ×, Y_2O_3).

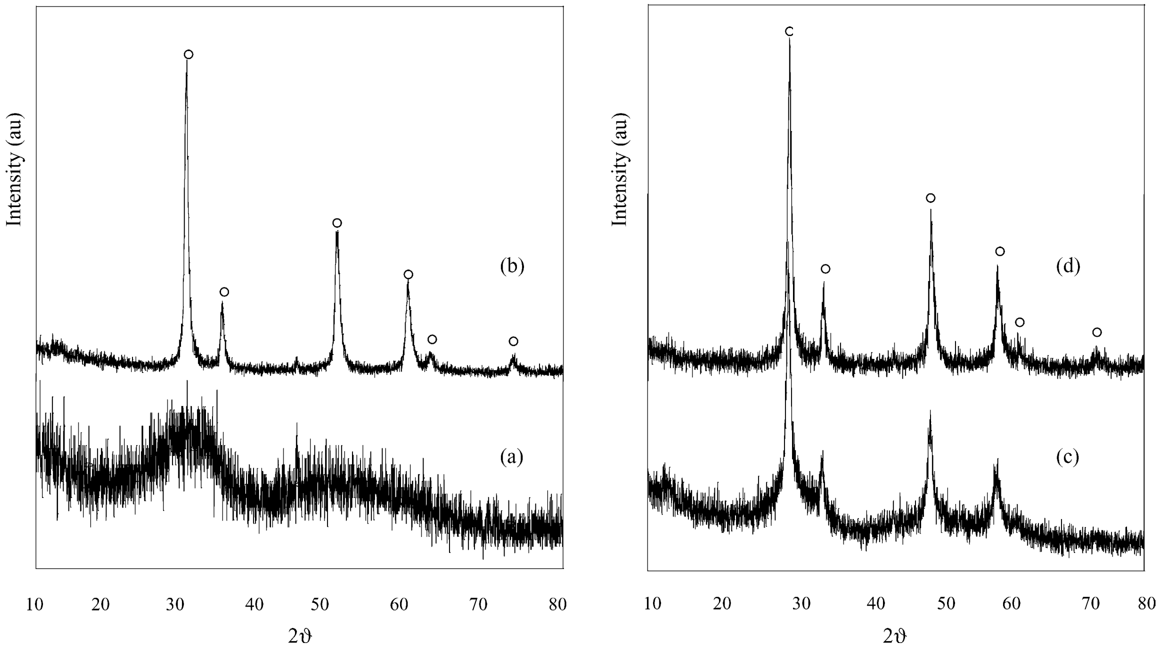

Fig. 2. XRD powder patterns of products synthesized by MHT at 110 °C for 1 h in the presence of dilute (a) and concentrated (d) solution of the mineralizer, and of the corresponding products after an additional treatment at 150 °C for 2 h in the presence of dilute (b) or concentrated (c) solution of the mineralizer (○, c-ZrO_2).

crystalline Y_2O_3, and of the corresponding products obtained by CHT at 110 °C for 72 h in the presence of dilute (0.2 M) or concentrated (2.0 M) solution of the mineralizer. The characteristic XRD peaks of the crystalline Y_2O_3 and the amorphous band of ZrO_2 xerogel are present in the starting mixture (Fig. 1a). Well crystallized cubic-ZrO_2 and a small amount of monoclinic-ZrO_2 are present in the product synthesized in the presence of the dilute mineralizer solution (Fig. 1b), whereas only c-ZrO_2 crystallizes from the concentrated solution (Fig. 1c).

The XRD powder patterns of the corresponding products synthesized by MHT, are shown in Fig. 2. After 1 h of treatment at 110 °C, an amorphous product results in the presence of the dilute solution of the mineralizer (Fig. 2a). The absence of the XRD peaks of starting crystalline Y_2O_3 must be outlined and the formation of an amorphous Y_2O_3–ZrO_2 solid solution must be considered. In fact, taking into account the pH and the volume of the mineralizer solution, an eventual dissolution of the crystalline Y_2O_3 in the mineralizer solution must be excluded. After 1 h of treatment at 110 °C in the presence of concentrated solution, a partial crystallization of zirconia results (Fig. 2c). In the presence of both dilute or concentrated solutions of the mineralizer, a full crystallization of c-ZrO_2 results after an additional MHT at 150 °C for 2 h (Fig. 2b and d). Unlike the product obtained by CHT and in dilute solution of mineralizer, no trace of monoclinic ZrO_2 has been detected in the corresponding product synthesized by MHT.

The crystal sizes and surface area of c-ZrO_2 of the full crystallized products obtained by both CHT and MHT, respectively, are summarized in Table 1. Even though a higher temperature (150 °C) to crystallize the zirconia has been adopted by the MHT in respect to the lower one used with the CHT (110 °C), comparable values of the crystal sizes and of the surface area of the corresponding products have been measured. It is confirmed that the hydrothermal treatments performed in the presence of the dilute solution of the mineralizer, favour the crystallization of products with larger crystal sizes.

After an adjustment of the pH of the aqueous suspensions at 6.8, i.e. below the isoelectric point of 7.3 as determined in water for these type of powders,[21] the suspensions were treated with PVA.

The adsorption of PVA onto the surfaces of polycrystalline powders has been confirmed by DTA–TGA and by the IR spectra as reported in Fig. 3, in which an as synthesized

Table 1
Crystal sizes (nm) and surface area (m^2/g) of full crystallized products synthesized by CHT and MHT, respectively

	Concentration of the mineralizer solutions (M)			
	0.2	2.0	0.2	2.0
CHT (110 °C), 72 h	16 nm	13 nm	89 m^2/g	114 m^2/g
MHT (110 °C, 1 h) → (150 °C, 2 h)	15 nm	13 nm	93 m^2/g	118 m^2/g

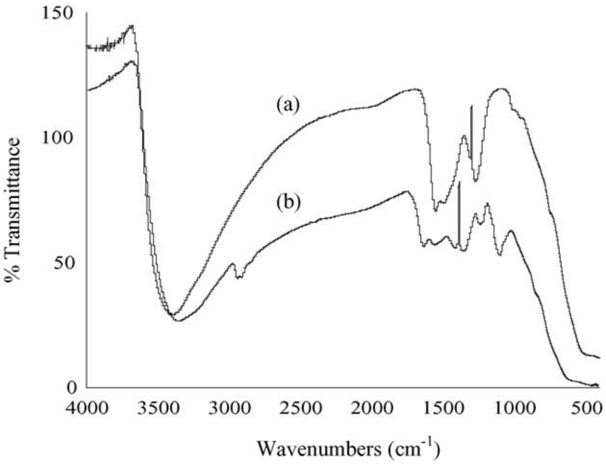

Fig. 3. FTIR spectra of the full crystallized product obtained by CHT at 110 °C for 72 h in the presence of the concentrated solution of the mineralizer (a), and of the corresponding PVA-adsorbed product (b).

product and the corresponding PVA adsorbed powder are compared. A weight loss increase of order of 9% has been measured after the treatment with PVA whose presence is confirmed by FTIR spectra reported in Fig. 3 in which the as-synthesized product and the corresponding PVA adsorbed powder are compared. The presence of additional adsorption peaks at 2930–2938 cm^{-1} and 1094 cm^{-1} for the treated powder, attributable to the vibrations of C–H and C–O, respectively, confirms the PVA adsorption. It must be outlined that the adsorption of PVA does not significantly improve the stability of suspensions against the flocculation in water. The as synthesized powders were directly stirred under ultrasonic agitation for 30 min. Different stabilities of the corresponding suspensions have been detected. More stable suspensions resulted, in fact, for the powders synthesized by CHT and MHT, respectively, and in the presence of the concentrated solution of the mineralizer, whereas the powders crystallized in the presence of the concentrated solution of the mineralizer gave less stable suspensions against the flocculation. Consequently the treatment with PVA was eliminated, and the powders have been directly submitted to ultrasonic treatment for 30 min in aqueous solution of PEG.

With the sol–gel technique, homogeneous films were obtained at low and high withdrawal-coating speed, but numerous cracks were detected after the thermal treatment at 600 °C, especially for thick films (Fig. 4a) Thin or thick films obtained from the suspensions containing the powders synthesized in the presence of the diluted solution of mineralizer and thermally treated, resulted free of cracks. Apart from the presence of some small aggregates (Fig. 4b), a homogeneous texture still appears at higher magnification (Fig. 4c). A less homogeneous texture characterized by the presence of several aggregates relatively bigger in sizes results for the powders crystallized in the presence of concentrated solution of the mineralizer (Fig. 4d). Nevertheless the different temperature adopted in the hydrothermal treatments performed by CHT and MHT, respectively, the type of hydrothermal treatment does not affect significantly the texture of the films.

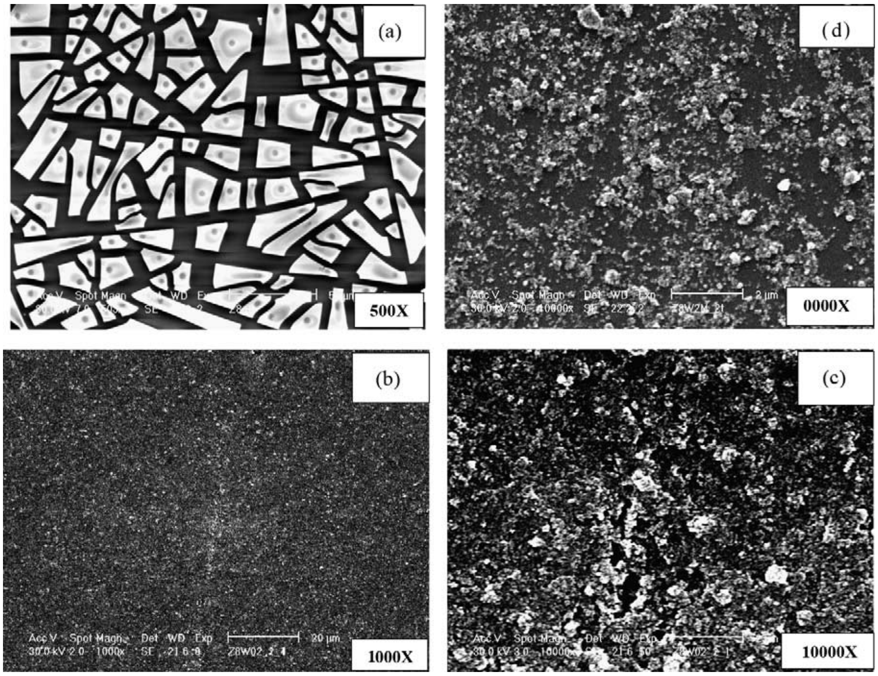

Fig. 4. SEM micrographs of thermally treated films at 600 °C: film by sol–gel technique (a), films by slurry coating of the powders synthesized by the MHT in dilute (b and c) or concentrated (d) solution of the mineralizer.

4. Conclusions

The thermal treatment at 600 °C of the homogeneous films deposited by the sol–gel technique, determines the formation of numerous cracks especially for thick films attributable to the high shrinkage of the gel on heating.

The stabilization of nanocrystalline suspensions against the flocculation requires preliminary treatments depending on the characteristics of the starting powders. 8Y-SZ powders synthesized in the presence of dilute solutions of the mineralizer and by CHT and MHT, respectively, do not require a preliminary treatment with a dispersant. The ultrasonic treatment of the aqueous suspension is, in fact, sufficient to produce stable suspension being the starting powders very weakly agglomerated. To favour the film formation by utilizing such powders, a treatment with PEG assisting the film formation is necessary nevertheless. On the contrary, less stable suspensions result by utilizing the powders synthesized in the presence of concentrated solutions of the mineralizer, in this case a scarce deposition of the powders and not homogeneous films result.

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