

Agglomeration of 3 mol% Y–TZP powders synthesized by hydrothermal treatment

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Abstract

Mechanical mixtures of zirconia gel and crystalline Y_2O_3 (3 mol%) have been hydrothermally treated at 110°C for 7 days in the presence of different mineralizer solutions. Taking the K_2CO_3/KOH molar ratio constant and equal 3, the total concentration of the mineralizer solutions was changed between 0.25 and 3.0 M. Predominant tetragonal (T) ZrO_2 , characterized by different crystal size and different degree of agglomeration resulted by changing the concentration of mineralizer solution. The crystallization rate of Y–TPZ based powders, as well as the texture of the corresponding sintered products, are discussed in terms of concentration of the mineralizer solutions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Agglomeration; Crystallisation rate; Hydrothermal processing; Mineralizer; ZrO_2

1. Introduction

Zirconia-based ceramics are receiving much attention in relation to their great technological interest. Typically stabilized zirconia with 3 mol% Y_2O_3 , 3Y–TZP ceramics, exhibit high strength and fracture toughness and find many increasing and demanding structural applications.^{1,2} Their mechanical performances are largely influenced by the processing procedures for the fabrication. The most important step in fabricating the Y–TPZ of desirable mechanical properties is represented by the quality of the base powders.^{3,4} Fine size, narrow size distribution and weakly agglomerated nanoscale primary particles represent successful features in fabricating a ceramic of desirable microstructure. Aqueous chemical processes are the most commonly used processing routes to produce better and cheaper Y–TZP powders. Monodisperse spherical powders can be prepared by homogeneous precipitation/co-precipitation of zirconia/zirconia-yttria as hydroxides followed by an aging step in which the nanoscale primary particles of resulting colloidal suspension are allowed to aggregate into micrometer-size spheres as aggregates. It is essential,

in this case, to avoid the formation of groups of firmly bound particles as agglomerates.⁵

Several papers have been published on the production of monodisperse zirconia particles by hydrolysis of alkoxides⁶ and thermal hydrolysis of zirconium salts.^{7–10} In many cases the so produced spherical particles have not been used for the high production cost connected to the use of extremely dilute solutions of zirconium salts. On the other hand the necessary calcination of hydrated and nanometer-size particles of zirconia-based powders promotes, in many cases, the formation of hard agglomerates.

Hydrothermal synthesis is a simple process to prepare, in a single step, homogeneous, mouldable, fine and weakly agglomerated powders. In addition it is possible to prepare large quantities of the product. Several papers have reported the hydrothermal synthesis of yttrium-doped zirconia powders.^{11–15} By hydrothermal crystallization of co-precipitated (Y,Zr) hydroxide gel at ~100°C in an open vessel under KOH conditions (pH~14), Tsukada et al.¹⁴ obtained cubic or tetragonal Y– ZrO_2 with 6 mol% yttrium. The resulting powders were fine primary particles ~10 nm in size, with a surface area of 170–220 m²/g. In this case, no detail on the full crystallization of products was specified. In our recent results,¹⁵ ultrafine powders of ZrO_2 – Y_2O_3 solid solutions have been synthesized by hydrothermal treatment of mechanical mixtures of zirconia gel and

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crystalline Y_2O_3 at $110^\circ C$ and in the presence of various mineralizers. The simultaneous presence of the alkaline carbonate and alkaline hydroxide in the mineralizer solution demonstrated that it is essential to the crystallization–stabilization of zirconia. Dell'Agli et al.¹⁶ observed the incorporation of some Li^+ or Na^+ in the crystalline and metastable ZrO_2 hydrothermally produced from zirconia gel in the presence of $LiOH$ and $NaOH$ solutions as mineralizers, unlike the crystalline ZrO_2 obtained in the presence of KOH and $(CH_3)_4NOH$, respectively.

The aim of this work concerns the hydrothermal synthesis and characterization of 3 mol% Y_2O_3 – ZrO_2 using a mechanical mixture of ZrO_2 gel and commercial Y_2O_3 in the presence of increasing concentrations of $(KOH + K_2CO_3)$ as mineralizer solutions.

2. Experimental procedure

Zirconia gel, precipitated from GR grade $ZrCl_4$ (Merck, Germany) solution with ammonia, Y_2O_3 (99.999 purity; Fluka Chemie AG, Switzerland), KOH and K_2CO_3 both GR grade (C. Erba, Italy), were employed for the hydrothermal treatments. The ZrO_2 content of gel precursor was determined by thermogravimetric analysis (TGA) with a Netzsch Thermoanalyzer STA 409. The hydrothermal treatments of mechanical mixture of 3 mol% Y_2O_3 – ZrO_2 gel were performed in the presence of various mineralizer solutions containing both KOH and K_2CO_3 . Taking the K_2CO_3/KOH molar ratio constant and equal to 3, the total concentration levels for mineralizer solutions were 0.25, 0.50, 1.0, 2.0 and 3.0 M. A solid/liquid ratio equal to 1/20 was adopted for each suspension which was transferred to a half-filled, sealed Teflon vessel. All the vessels were positioned in an air-thermostated oven at $110^\circ C$ and rotated at 25 rpm. After a reaction time of 7 days, the products were filtered and repeatedly washed with distilled water to remove K^+ ions, and dried on silica gel.

XRD was performed using a X'PERT diffractometer of Philips and $Cu-K_\alpha$ radiation to detect the crystalline phases of products. Primary particle size of tetragonal ZrO_2 (T - ZrO_2) was calculated by the Sherrer formula by measuring the half width of $(111)_T$ diffraction peak with a software for the correction of $\alpha_1\alpha_2$ overlap and by using polycrystalline silicon for the correction of instrumental broadening. The crystalline content of T - ZrO_2 was determined by adopting the intensity relationship:

$$\frac{I(111)_T}{I(111)_T + I(\bar{1}\bar{1}\bar{1})_M + I(111)_M}$$

where M and T refer to monoclinic and tetragonal ZrO_2 , respectively. The specific surface area of products

was determined by the BET method using a Gemini of Micromeritics and utilizing nitrogen as adsorbate, after drying the powders under vacuum at $60^\circ C$. The morphology of both the powders and the corresponding sintered products was analyzed by scanning electron microscopy (SEM) using a Philips model XL30. One side of the sintered products was initially ground using a $30\ \mu m$ diamond wheel and then polished to a $1\ \mu m$ diamond finish. To reveal the microstructure, the sintered products were also thermally etched at $1350^\circ C$ for 1 h.

3. Results and discussion

Hydrothermal crystallization of mechanical mixtures of zirconia gel and crystalline Y_2O_3 (3% mol) in the presence of increasing concentrations of $(KOH + K_2CO_3)$ mineralizer solutions resulted mainly in tetragonal (T) zirconia as shown in Fig. 1. A small amount of well crystallized monoclinic (M) phase has been detected in products synthesized in 0.25 and 0.50 M solutions of mineralizer. However, XRD patterns of Fig. 1 do not indicate the full crystallization of the gel precursor. As zirconia gel shows in DTA a very sharp and significant exothermic peak at about $430^\circ C$, the presence of uncrystallized zirconia gel in the products may be evaluated by

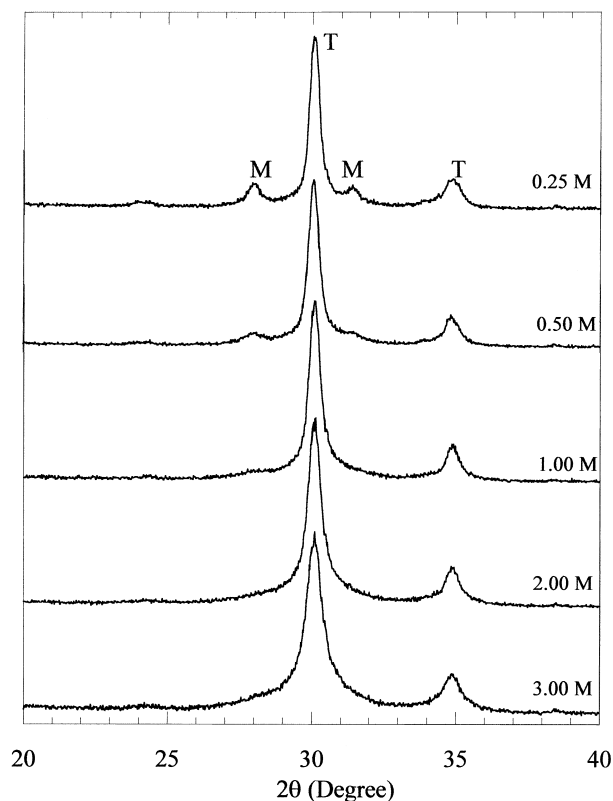


Fig. 1. XRD patterns of products hydrothermally synthesized at $110^\circ C$ for 7 days from a mechanical mixture of zirconia gel and crystalline Y_2O_3 (3 mol%) in the presence of different concentrations of mineralizer ($KOH + K_2CO_3$) solutions.

this exothermic signal. By comparing the DTA curves of all the products, the presence of a small exothermic peak, especially for products synthesized in concentrated solutions of mineralizer, is indicative of the incomplete crystallization of the zirconia gel precursor (Fig. 2). The absence of such signal in the products obtained in 0.25 and 0.50 M, shows the full crystallization of the corresponding products.

Phases present, specific surface area, % weight loss, % content and crystal size of T phase in products obtained by hydrothermal treatment at 110°C for 7 days of mechanical mixture of 3 mol% Y_2O_3 - ZrO_2 gel as a function of concentration ($KOH + K_2CO_3$) mineralizer are gathered in Table 1. Fully and well crystallized products are obtained in diluted solutions of ($KOH + K_2CO_3$) mineralizer according to the effect of mineralizer concentration on the nucleation and crystal growth process during the crystallization-stabilization of zirconia gel¹⁶ in the presence of ($NaOH + Na_2CO_3$) mineralizer. The results of surface-area measurements shown in Table 1, are consistent with the measured crystal sizes of the predominant T- ZrO_2 of products. The smaller surface areas of products obtained in 0.25 and 0.50 M, respectively, agree, in fact, with the corresponding higher crystal sizes of T phase. The higher surface areas of products obtained instead at higher mineralizer concentrations are consistent with both the

smaller crystal sizes of the corresponding T phase and the presence of traces of uncrystallized zirconia gel.

The total weight losses of products measured at 1100°C indicate increasing values for the products hydrothermally synthesized in the presence of increasing concentration of mineralizer (Table 1), while lower values result for fully crystallized products obtained in 0.25 and 0.50 M, respectively.

Adopting a heating rate of 5°C/min, the uncompact and hydrothermally synthesized powders have been calcined for 1 h at increasing temperatures ranging between 600 and 1500°C. After the calcination, the products resulted in mixtures of T and M phases. The resulting and predominant amount of T- ZrO_2 has been reported in Fig. 3 as a function of both the temperature of calcination and the mineralizer concentration. In the presence of more concentrated solutions of mineralizer, the corresponding calcined products resulted in being richer in T- ZrO_2 content (>90%), while a slightly poorer content resulted in calcined products synthesized in less concentrated solutions of the mineralizer (~85%). The fraction of uncrystallized zirconia gel, present in the products hydrothermally synthesized in more concentrated solutions, justifies the formation of some M phase during the calcination. Zirconia gel crystallizes, in fact, into the metastable T form at 430°C and recrystallizes into the stable M- ZrO_2 at higher temperature of thermal treatment. No significant difference in the M phase content results between calcined and corresponding uncalcined products synthesized in less concentrated solutions of the mineralizer.

The crystal sizes of the prevalent T- ZrO_2 of all uncalcined and calcined products have also been measured and reported in Fig. 4. It is apparently evident that the crystal growth rate of uncompact powders during heating and isothermal treatment is independent from the nature of starting powders. Fig. 5 shows the

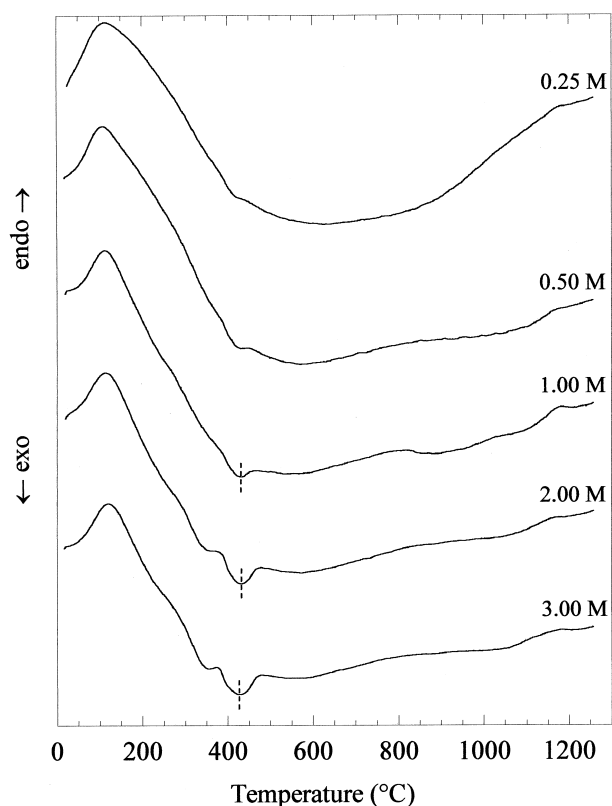


Fig. 2. DTA curves of products listed in Fig. 1.

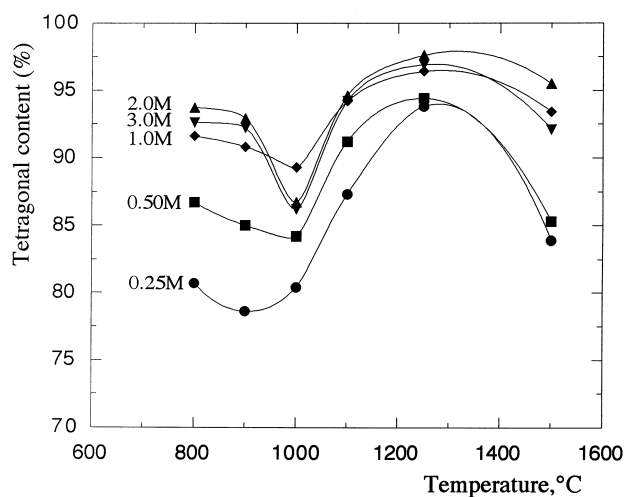


Fig. 3. Tetragonal zirconia content of products listed in Fig. 1 after calcination at increasing temperatures.

Table 1

Phases present, surface area, % weight loss, % content and crystal size of tetragonal ZrO_2 of products obtained by hydrothermal treatment at $110^\circ C$ for 7 days of mechanical mixture of 3 mol% Y_2O_3 - ZrO_2 gel as a function of concentration ($KOH + K_2CO_3$) mineralizer^a

Total molarity ($KOH + K_2CO_3$)	Phases	% Content of T phase	Crystal size (nm) of T phase	Surface area (m^2/g)	Weight loss (%)
0.25	T, M	85	23	45	8.0
0.50	T, M	89	21	72	9.6
1.0	T, (A) ^b	100 ^c	19	90	10.7
2.0	T, (A)	100 ^c	16	110	12.3
3.0	T, (A)	100 ^c	14	132	13.9

^a A, M and T are amorphous, monoclinic and tetragonal ZrO_2 , respectively.

^b Round brackets indicate the presence of traces of phase.

^c Content % with respect to the crystalline phases.

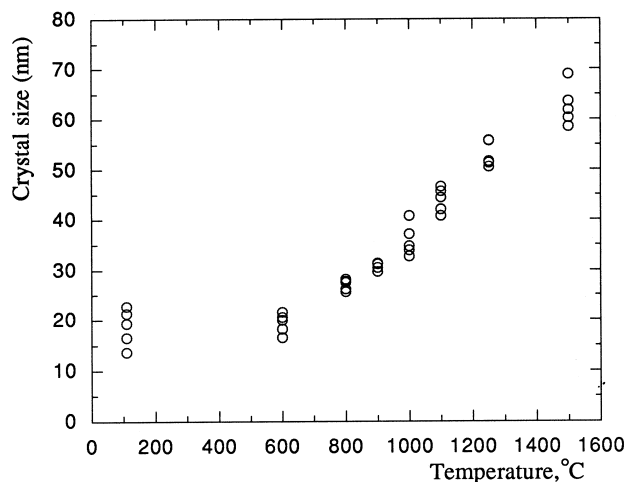


Fig. 4. Crystal size of T- ZrO_2 present in the products listed in Fig. 3.

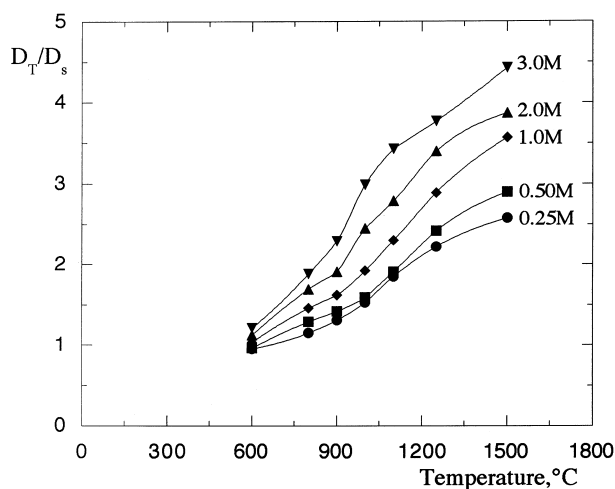


Fig. 5. D_T/D_s ratio of products hydrothermally synthesized in the presence of different concentrations of mineralizer solution as a function of temperature of calcination. (D_T) is the crystal size of T- ZrO_2 , measured at the selected temperature of calcination, (D_s) is the crystal size of T- ZrO_2 directly measured on the corresponding and hydrothermally synthesized product.

relation obtained by plotting, as a function of temperature of calcination, the ratio between the crystal size of T- ZrO_2 , measured for each product at the selected temperature of calcination (D_T), and the crystal size of the same T phase, directly measured on the corresponding and hydrothermally synthesized product (D_s). The influence of starting powders on the ratio D_T/D_s , in this case, appears significant. At a same temperature of calcination, higher D_T/D_s values result, in fact, for products synthesized in more concentrated solutions of mineralizer. The increase of such a ratio at increasing temperature of thermal treatment can not only be explained in terms of crystal growth on sintering, as the starting powders were not previously compacted. Such an increase may be also justified in terms of a different degree of agglomeration of starting powders; i.e. by the presence of groups of firmly bound primary particles as agglomerates. An indubitable statement allows us to declare that the groups of firmly bound (agglomerated) primary particles will densify more rapidly than those weakly bound in the aggregates, which in turn will densify more rapidly than the primary particles of adjoining aggregates. Considering the D_T/D_s value as a measure of the degree of agglomeration of the starting powders, a low degree of agglomeration must be expected for powders hydrothermally synthesized in diluted solutions; i.e. in 0.25 and 0.50 M, respectively. These powders are characterized, in fact, by a D_T/D_s value of about 2.5 at temperatures of calcination of $1500^\circ C$. This value suggests that at least 3 firmly bound primary particles are on average present in the corresponding powders synthesized in diluted solutions of mineralizer. The number of such agglomerated primary particles remarkably increases for powders synthesized in more concentrated solutions of mineralizer as the D_T/D_s value ranges between 3.5 and 4.5. It must be also into account that the starting crystal size of T- ZrO_2 obtained in 0.25 M is 23 nm, while that one obtained in 3.0M is 14 nm. In addition a full crystallization has been detected in diluted solutions, whereas an incomplete crystallization resulted in concentrated solutions of

mineralizer. These findings agree with the effect of basic mineralizers on the crystallization rate of zirconia gel¹⁷ under hydrothermal conditions. Such rate increases, in fact, with the concentration of basic mineralizer. For a selected basic mineralizer, in this case (KOH + K₂CO₃), there is a minimum concentration at which a minimum driving force for the full structural rearrangement of gel corresponds and, consequently, for its full crystallization. However, in this circumstance a very low rate of structural rearrangement as well as nucleation and consequent crystallization of gel must be expected as confirmed by the higher crystal sizes of T-ZrO₂ detected in the diluted solutions. In these conditions the low condensation reaction rate of structural hydroxyl groups of embryonic particles of gel favours the formation of high crystal-sizes and scarcely agglomerated primary particles. On the contrary, a high condensation reaction rate favours the formation of low crystal-size and partly agglomerated particles as experimentally observed in powders synthesized in concentrated solutions of mineralizer.

Analogous results have been detected by adopting (NaOH + Na₂CO₃) solutions as the mineralizer during the hydrothermal treatment of the same mechanical mixture of zirconia gel and 3 mol% Y₂O₃. Also in this case T-ZrO₂ resulted from the predominant phase of hydrothermally synthesized products. The crystal sizes of T-phase measured on powders hydrothermally synthesized and on the corresponding calcined products at 600 and 1100°C, respectively, are reported in Fig. 6 as a function of (NaOH + Na₂CO₃) concentration. The progressive diminution of crystal size of T-ZrO₂ in products obtained at increasing concentration of the mineralizer (curve *a*) is confirmed. The curve *b*, referring to T-phase of products calcined at 600°C, shows a doubling of the crystal size values, unlike the behavior detected for the corresponding calcined products obtained with (KOH + K₂CO₃) solutions. The curve *c* of the calcined products at 1100°C shows a further increase of crystal sizes especially for products obtained at higher concentration of mineralizer. By plotting the D_T/D_s values at 600 and 1100°C (Fig. 7), respectively as a function of mineralizer concentration, relatively higher values resulted in this case in comparison to the observed values for products obtained in (KOH + K₂CO₃) solutions (Fig. 4). The degree of agglomeration of powders appears, in this case, significantly higher than those obtained in (KOH + K₂CO₃) solutions. Such findings agree with the higher crystallization rate of zirconia gel in the presence of basic MOH mineralizer with lower cationic radius of M⁺, i.e. $r_{Na^+} < r_{K^+}$.¹⁶ On the other hand the detected incorporation of some Na⁺ in the products crystallized in the presence of NaOH mineralizer might favour the formation of firmly bound primary particles and, consequently, the higher degree of agglomeration of such powders as indicated by the higher D_T/D_s values.

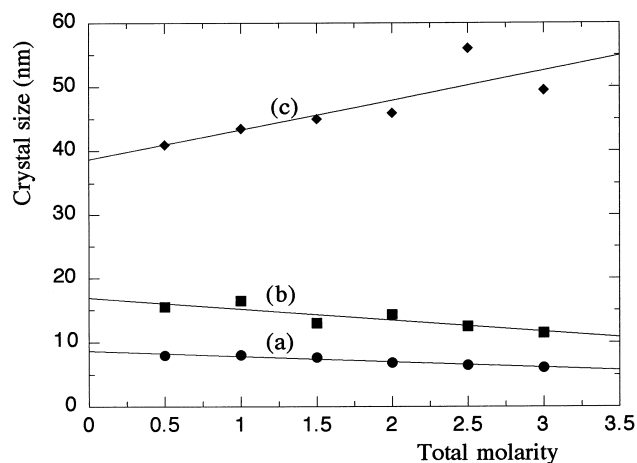


Fig. 6. Crystal size of T-ZrO₂ of products hydrothermally synthesized in the presence of increasing concentrations of (NaOH + Na₂CO₃) mineralizer: uncalcined products (curve *a*); after calcination at 600°C (curve *b*); after calcination at 1100°C (curve *c*).

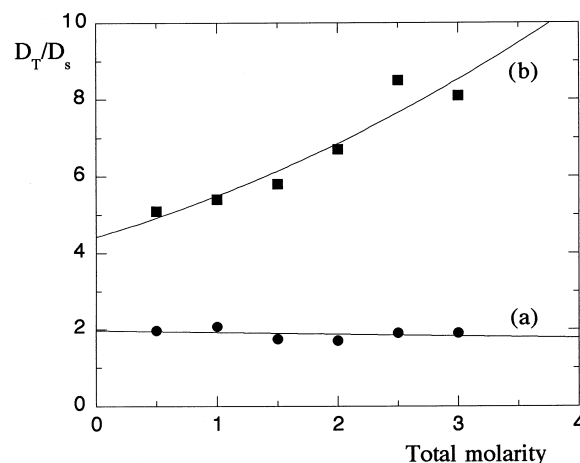


Fig. 7. D_T/D_s ratio of products listed in Fig. 6 as a function of (NaOH + Na₂CO₃) concentration. D_T is the crystal size of T-ZrO₂ of products calcined at 600°C (curve *a*) and at 1100°C (curve *b*), respectively; D_s is the crystal size of T-ZrO₂ directly measured on the corresponding and hydrothermally synthesized products.

The microstructure of powders synthesized in the presence of (KOH + K₂CO₃) mineralizer and observed by SEM results as micrometer-size aggregates. By ultrasonic treatment for 2–3 min, these aggregates collapse and disperse in ethyl alcohol to form a translucent sol. In spite of the higher crystal size, longer sedimentation times resulted for less agglomerated powders, i.e. for products synthesized in the presence of diluted solutions of mineralizer, while shorter sedimentation times have been detected for powders synthesized in concentrated solutions. Such behaviour indirectly confirms the effect of the mineralizer concentration on the degree of agglomeration of the corresponding products.

With the purpose to verify the effect of the different degree of agglomeration of products on their microstructure after sintering, the powders were previously

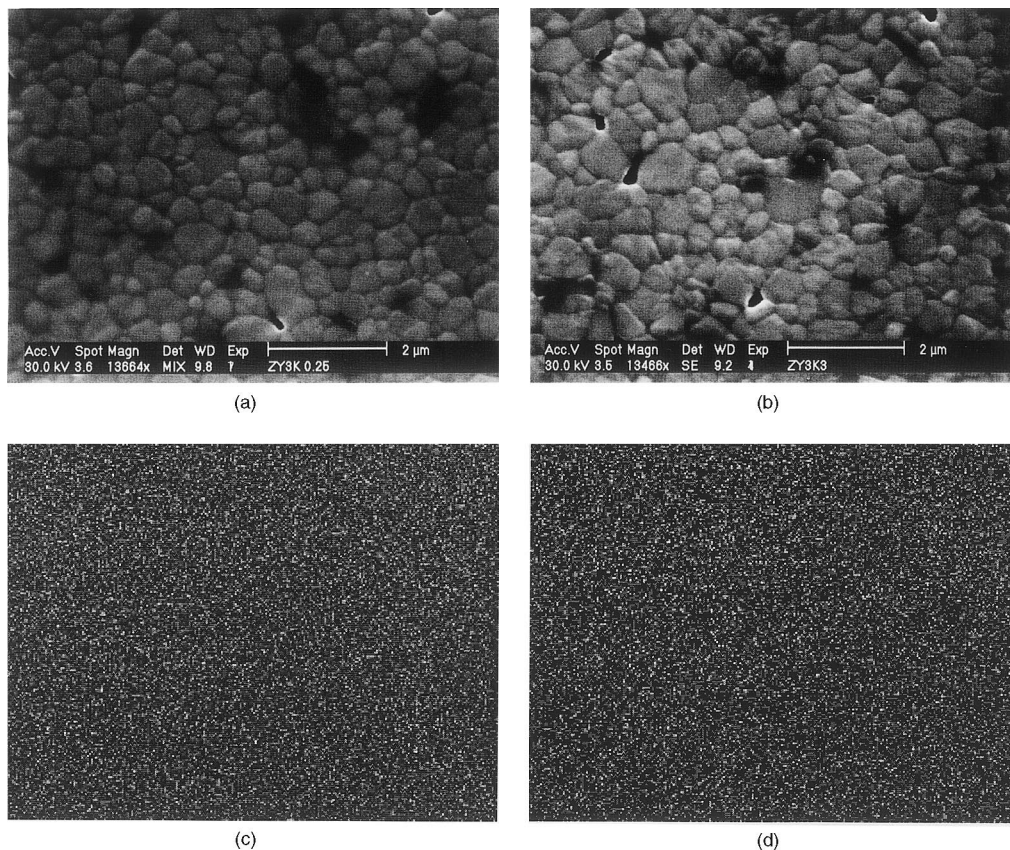


Fig. 8. SEM micrographs of products obtained in 0.25 M (a) and 3.0 M (b) concentration of mineralizer, respectively, after calcination at 600°C and sintering for 3 h at 1500°C. Micrograph (c) and (d) reveals the corresponding electron microprobe maps of yttrium distribution.

calcined at 600°C for 2 h, compacted first uniaxially at 40 MPa and then isostatically at 150 MPa obtaining cylindrical pellets having height = 5 mm and diameter 10 mm. Adopting a heating rate of 5°C/min, the corresponding pellets have been sintered at 1500°C for 3 h. SEM pictures of polished and thermally etched surfaces of sintered products are shown in Fig. 8. Less agglomerated powders, obtained in diluted solution of mineralizer, exhibit an uniform grain structure (Fig. 8a) whereas a less uniform grain structure (Fig. 8b) exhibit the more agglomerated powders synthesized in the presence of concentrated solutions of mineralizers. Electron microprobe maps of the sintered powders characterized by either homogeneous or heterogeneous grain structure reveal an uniform yttria distribution. Such findings show that the hydrothermal treatment favours an uniform distribution of yttria in the grains of different size of powders unlike the Y-TZP powders prepared as gelatinous coprecipitates.¹⁸

4. Conclusions

The hydrothermal treatment of mechanical mixtures of zirconia gel and 3 mol% crystalline Y₂O₃ in the pre-

sence of solutions containing (KOH + K₂CO₃) as mineralizer, results in crystallization–stabilization of predominant tetragonal ZrO₂. Diluted solutions of the mineralizer promote the formation of fully crystallized products characterized by higher crystal size, while in concentrated solutions an incomplete crystallization of gel and tetragonal ZrO₂ with lower crystal sizes resulted. Such results have been related to the increasing rate of structural rearrangement as well as nucleation and consequent crystallization–stabilization of zirconia gel at increasing concentration of mineralizer.

The crystallization rate of zirconia gel also affects the degree of agglomeration of the primary particles of hydrothermally synthesized products. By comparing the crystal size of T–ZrO₂, measured for each uncompact product at a selected temperature of calcination (D_T), and the crystal size of the same T phase, directly measured on the corresponding and hydrothermally synthesized product (D_s), increasing D_T/D_s ratio have been detected for products synthesized in the presence of increasing concentration of mineralizer. The different degree of agglomeration of powders affects the microstructure of the corresponding sintered ceramics. A homogeneous texture with narrow size distribution of grains results for products obtained in diluted solutions

of mineralizer, while a less homogeneous texture results for products synthesized in concentrated solutions of mineralizer.

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