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Low temperature hydrothermal synthesis of ZrO_2-CaO solid solutions

G. DELL'AGLI, G. MASCOLO
Dipartimento di Meccanica, Strutture, Ambiente e Territorio-Laboratorio Materiali, Universita' di Cassino, via G. Di Biasio 43, 03043 Cassino (FR), Italy
E-mail: mascolo@ing.unicas.it

Nanosized powders of ZrO_2-CaO solid solutions have been synthesized by hydrothermal treatment at 110°C. Amorphous hydrous ZrO_2, CaO freshly prepared by thermal decomposition of $CaCO_3$ and MOH (M = Na, Li) mineralizer solutions were employed as precursors for the hydrothermal synthesis. Calcia-stabilized zirconia (CSZ) with different CaO content and characterized by different crystal sizes have been produced by changing the hydrothermal treatment temperature, the reaction time and the mixture composition of precursors. The combined effect of both MOH and CaO on the crystallization-stabilization of zirconia at low temperature of hydrothermal treatment is discussed.

1. Introduction

Wet-chemical methods produce ZrO_2 solid solutions powders characterized by high purity, high degree of compositional homogeneity and fine crystallite sizes [1–8]. Nevertheless, such characteristics do not always ensure an appropriate sinterability. A reduced strength, in fact, must also result between crystallites within the agglomerates and between the agglomerates [9–13]. To reduce such bonding strengths, some preliminary treatments have been proposed before the precalcination treatment so favouring the formation of uniform pore-size distribution compacts [14–16]. Among such preliminary treatments, the more simple and less expensive method appears to be the hydrothermal treatment.

CaO-stabilized ZrO_2 (CSZ) powders were firstly and hydrothermally prepared at temperatures between 200–250°C [17]. Soft agglomerates of CSZ powders, hydrothermally synthesized between 220 and 260°C, resulted easy to sinter to high densities at low temperatures [18]. Further studies showed that the crystallization of zirconia gel depends on both mineralizer solution and the conditions of the thermal treatment [19–21]. Monoclinic and metastable tetragonal zirconia have been produced, in fact, by hydrothermal treatment of zirconia gel with several mineralizers. Amorphous ZrO_2-MgO coprecipitates just after crystallization produced unstable cubic solid solutions which, by extended thermal treatment, decomposed to MgO plus monoclinic zirconia [2, 22].

We report a systematic study on the hydrothermal crystallization of CaO-ZrO_2 system at low temperature by using MOH (M = Na, Li) mineralizer solutions.

2. Experimental procedure

ZrO_2 gel, CaO freshly prepared and MOH (M = Na, Li) solutions were employed as precursors for the hydrothermal synthesis.

Amorphous zirconia-based precursor was precipitated from GR grade $ZrCl_4$ (Merck, Germany) solution with ammonia, filtered and repeatedly washed with distilled water until removal the chloride ions. The ZrO_2 content of such precursor was determined by thermogravimetric analysis (TGA). CaO was produced by thermal decomposition at 950°C of GR grade $CaCO_3$ (C. Erba, Italy). GR grade NaOH and $LiOH \cdot H_2O$ (C. Erba, Italy) were the bases for the preparation of mineralizer solutions. The concentration level of the solutions was ranged from 0.01 to 3.0 M. Many different suspensions with the mol% CaO content changing in a wide range of composition up to 45% were prepared.

The temperatures of hydrothermal treatments were 80, 110 and 140°C, respectively and a solid/liquid ratio equal to 1/40 was adopted. The reaction time was on average 7 days, but in some cases shorter and longer durations were also adopted. The precursors were transferred to half-filled and sealed Teflon vessels (500 mm^3). The vessels were rotated in air thermostated oven for selected reaction times. After the hydrothermal treatment, the products were filtered and repeatedly washed with distilled water to remove M^+ ions, and dried on silica gel.

The products were characterized by X-ray powder diffractometry (XRD) using a Philips PV 1730 diffractometer and Cu K_α radiation. The thermal behaviour of the products was investigated by simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a Netzsch thermoanalyzer mod. STA 409, α-Al_2O_3 as reference and a 10°C min^{-1} heating rate. The specific surface area of products was determined by the BET method using a Gemini of Micromeritics and utilizing nitrogen as adsorbate after drying at 60°C.

3. Results and discussion

The prepared stock of ZrO_2-based precursor resulted amorphous material according to XRD, showed in DTA a very sharp exothermic peak of crystallization into tetragonal zirconia at 430°C and gave in TGA a weight loss of 23%.

3.1. Hydrothermal treatments of ZrO_2 gel with mineralizer solutions

The phases present of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days as a function of various mineralizer solutions are shown in Table I. The treatments in distilled water, 0.01 M NaOH and 3 M NH_4OH resulted in an amorphous product, while crystalline products have been revealed in 0.05, 0.10, 0.50, 1.0 and 3.0 M NaOH. A mixture of amorphous, monoclinic and tetragonal zirconia has been obtained with 0.05 M, while a fully crystallized mixture of monoclinic and tetragonal zirconia resulted in 0.1 M. The test carried out in 0.5 M resulted in a mixture of traces of uncrystallized product, monoclinic and tetragonal zirconia with the prevalent content of the last form. Cubic zirconia crystallized in 1.0 M and 3.0 M NaOH, respectively. Only in the last mineralizer solution, a fully crystallized cubic form was revealed. The semicrystalline tetragonal zirconia observed upon ageing of zirconia gel in 1.0 M NaOH [23] partly supports such findings, while a good agreement appears with other results [24].

The weight loss, determined by TGA, of the same products obtained at increasing alkalinity of the mineralizer solution are reported in Fig. 1. The minimum in the curve corresponds to the fully crystallized product obtained in 0.1 M NaOH. An analogous trend for the specific surface area of the same products at increasing alkalinity has been observed and is given in Fig. 2.

TABLE I Phases present, surface area and % weight loss of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days as a function of mineralizer solution

Mineralizer	Phases	Surface area (m^2/g)[a]	Weight loss (wt%)[b]
Distilled water	Amorphous	275	21.9
NH_4OH (3.0 M)	Amorphous	273	20.5
NaOH (0.01 M)	Amorphous	274	21.9
NaOH (0.05 M)	Amorphous, (M), (T)	202	8.0
NaOH (0.10 M)	M, T	90	7.5
NaOH (0.50 M)	(Amorphous), T, (M)	73	10.0
NaOH (1.0 M)	(Amorphous), C, (M)	95	10.4
NaOH (3.0 M)	C	122	13.6

M, T and C are monoclinic, tetragonal and cubic ZrO_2, respectively. Parentheses indicate the presence of only small amount of a phase.

[a] Surface area of untreated zirconia gel: 285 m^2/g.

[b] Weight loss of untreated zirconia gel: 23.0%.

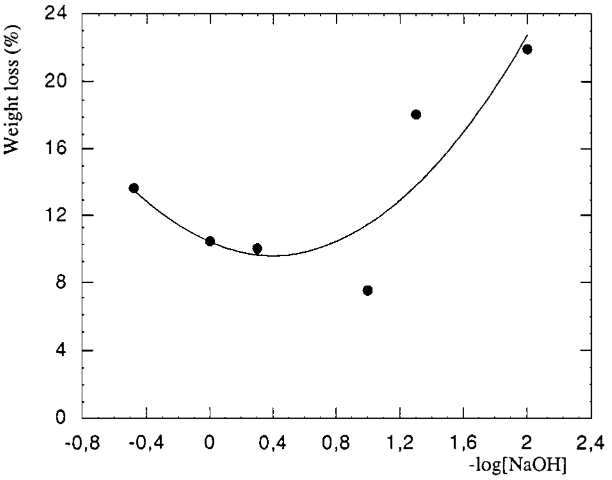

Figure 1 Weight loss of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days and in presence of increasing concentration of NaOH mineralizer.

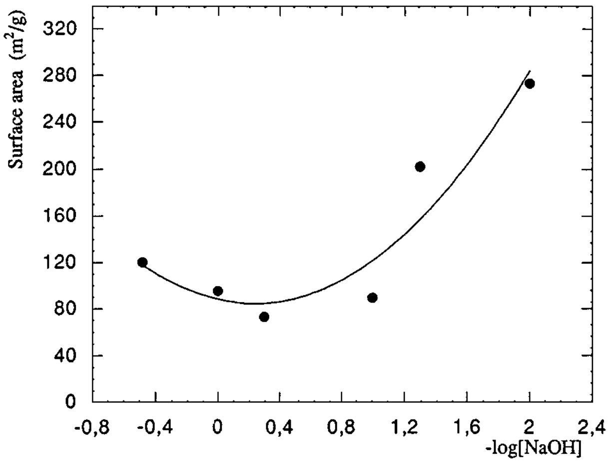

Figure 2 Surface area of same products of Fig. 1.

These results show that, taking the temperature and the duration of the hydrothermal treatment constant, the concentration of the mineralizer solutions influences the structural rearrangement of zirconia gel. Nishizawa *et al.* [24] observed the formation of cubic zirconia in NaOH solutions higher than 1 M and at 130–140°C and the crystal sizes decreased as the concentration of the NaOH mineralizer was increased.

The same results have been observed by comparing full width at half maximum (FWHM) peaks of cubic zirconia synthesized in 1.0 M and 3.0 M NaOH, respectively. Nishizawa *et al.* suggested that Na^+ (and OH^-), adsorbed on the gel, ruptured the Zr-O-Zr bridges with collapse and dehydration of structure with consequent formation of cubic zirconia. The strong base NaOH appears to favour instead the formation of oxo-bridgings between the non-bridging structural groups of the gel. The observed weight losses of products are due, in addition to the chemically coordinated and physisorbed water, respectively, to oxo-bridging and non-bridging hydroxyl groups. As the minimum in the curve of Fig. 1 corresponds to the minimum concentration of mineralizer solution able to promote the full crystallization of gel, the corresponding product is characterized by the minimum content of both water and hydroxyl groups. For alkalinity values higher than that at the minimum in the curve of Fig. 1, the corresponding increasing weight loss of products involves a relatively high content of water and hydroxyl groups, respectively. These results show that the alkalinity value and, in particular, the corresponding pH of the mineralizer solution significantly influences the structural rearrangement of gel and consequently its crystallization rate. The FWHM values measured for crystalline products increased with the increasing mineralizer concentration, so indicating that the crystal sizes decreased with the increasing mineralizer concentration. Taking FWHM as a measure of the nucleation rate, the progressive reduction in the crystal sizes of products at pH values higher than that at the minimum in the curve of Fig. 1, involves an increasing nucleation rate of gel and, consequently, a progressive reduction in the crystallite sizes of products. Such behaviour explains both the occurrence of the metastable forms of zirconia and the increasing weight loss.

All the products obtained by hydrothermal treatment in different concentrations of mineralizer solution, when thermally treated at temperature higher than 700°C, transform into monoclinic zirconia so showing the metastable character of both crystallized tetragonal and cubic forms.

3.2. Hydrothermal treatments of ZrO_2 gel in the presence of both CaO and MOH

ZrO_2-CaO solid solutions easily crystallized in different conditions of the hydrothermal treatment when NaOH and CaO were contemporaneously used in mixture with the amorphous precursor, whereas the crystallization-stabilization of zirconia failed when only CaO was used in mixture with the gel.

3.2.1. Effect of CaO content

The crystalline phases of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days in 0.25 M NaOH as a function of CaO content, are shown in Table II. Powders obtained from mixtures with CaO content up to 8 mol% contain solid-solutions of both monoclinic and tetragonal zirconia. The amount of the last form increases with increasing CaO content. Mixtures of monoclinic and cubic zirconia have been detected in the composition range between 8 mol and 15 mol% with the amount of the cubic form that increases by increasing CaO content. Cubic zirconia has been detected for CaO contents higher than 15 mol%. Free CaO, detected by XRD as $CaCO_3$ owing to the carbonatation of hydrated CaO, has been observed in powders with CaO content higher than 30 mol%. From phase equilibria in the ZrO_2-CaO system, the solubility of CaO in ZrO_2 is slightly higher than 20 mol% [25–27] at the eutectic temperature of 2250 ± 20°C. In this case, cubic ZrO_2 powders with CaO contents between 20 mol and 25 mol% have been observed. Such anomaly might be explained taking into account that the phase relations in the ternary system ZrO_2-CaO-H_2O are not the same of binary system ZrO_2-CaO as was observed for yttria-doped zirconia prepared by wet-method [28]. All the hydrothermally synthesized powders denoted, in fact, a broad endothermic peak in DTA curve at temperatures ranging between 130 and 150°C due to the loss of water followed by a further weight loss extending up to 500°C which has been attributed to the loss of residual hydroxyl groups.

The typical and sharp exothermic peak associated with the crystallization of amorphous zirconia resulted absent in fully crystallized samples. This peak has been advantageously utilized in checking the full crystallization of amorphous precursor. A further endothermic peak in DTA curve was observed at 750°C in powders synthesized from mixtures with CaO content higher than 30% mol. Such peak has been attributed to decomposition of $CaCO_3$ as confirmed by the corresponding weight loss in TGA curve.

3.2.2. Effect of concentration of mineralizer solution

Taking the conditions of hydrothermal treatment constant, the effect of MOH concentration on the crystallization-stabilization of ZrO_2-based phases has been also investigated. Poorly crystallized zirconia was detected in presence of alkalinity values lower than 0.01 M, while an increasing crystallization takes place in the composition range between 0.01 to 0.05 M LiOH. The crystallization degree of cubic ZrO_2 was almost the same in presence of LiOH concentrations higher than 0.5 M (Fig. 3). It is interesting to note that the type of alkaline cation of the mineralizer, LiOH or NaOH in this case, determines small differences in the crystallization of ZrO_2-based phases. This evidence indicates that the pH of the mineralizer is a primary factor in the crystallization-stabilization of zirconia.

The FWHM of the XRD peaks for cubic samples stabilized with 17% mol of CaO and obtained in the

TABLE II Phases present of products obtained by hydrothermal treatment of zirconia gel at 110°C for 7 days in 0.25 M NaOH as a function of CaO content

CaO content (mol %)	1	3	5	7	10	13	17	19	20	21	23	25	30	35
Phases	A T M	A T M	(A) T M	(A) C (M)	(A) C (M)	(A) C (M)	C	C	C	C	C	C	(B) C	B C

A and B are amorphous zirconia and calcite ($CaCO_3$), respectively; M, T and C are monoclinic, tetragonal and cubic ZrO_2, respectively. Parentheses indicate the presence of only small amount of a phase.

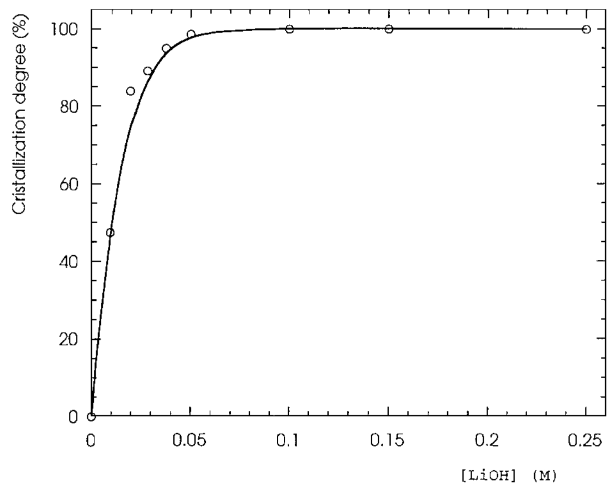

Figure 3 Crystallization degree of cubic stabilized samples (ZrO_2-17 mol% CaO) synthesized at 110°C for 7 days and in presence of increasing LiOH concentration of mineralizer solution.

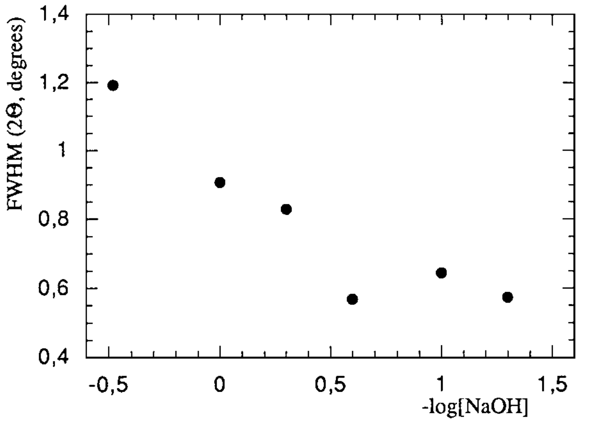

Figure 4 Variation of the FWHM of the (111) reflection peak for cubic samples (ZrO_2-17 mol% CaO) synthesized at 110°C for 7 days and in presence of increasing NaOH concentration of mineralizer solution.

presence of NaOH solutions with the composition ranging from 0.05 to 3.0 M NaOH, are shown in Fig. 4. The increasing values of FWHM with the increasing mineralizer concentration, indicate a corresponding decrease of the crystal sizes for the cubic forms so confirming the effect of the mineralizer concentration on the nucleation rate also during the crystallization-stabilization of zirconia.

3.2.3. Effect of both temperature and time of hydrothermal treatment

The temperature of the hydrothermal treatment also influences the crystallization of the products. In particular, both increasing crystal sizes and increasing crystallization degree have been observed by increasing the temperature of hydrothermal treatment especially when the temperature was changed from 80 to 110°C (Fig. 5). On the other hand, by adopting a same condition of hydrothermal treatment, i.e. temperature, reaction time and concentration of mineralizer, the cubic ZrO_2 powders are characterized by a decreasing crystallite size by increasing the mol% of CaO.

A further investigated parameter concerns the minimum duration of hydrothermal treatment to achieve the full crystallization-stabilization of ZrO_2. Fig. 6 shows the X-ray powder patterns of products obtained by hydrothermal treatment at increasing reaction times performed at 110°C on ZrO_2-17 mol% CaO and in presence of 0.25 M NaOH solution. As can be seen, the full crystallization of zirconia is completed after 48 hours of hydrothermal treatment.

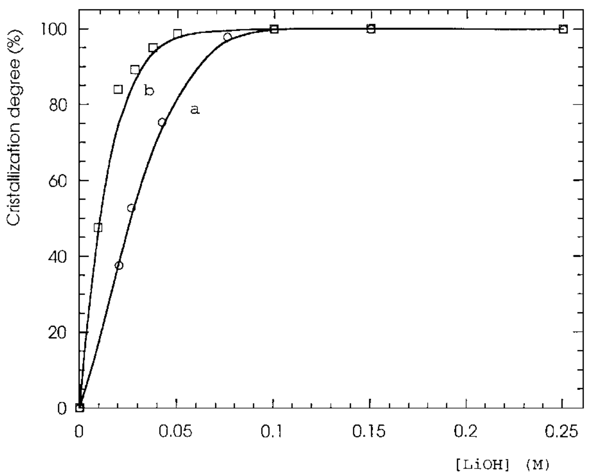

Figure 5 Crystallization degree of cubic samples (ZrO_2-17 mol% CaO) obtained after 7 days of hydrothermal treatment at 80°C (curve a) and at 110°C (curve b), respectively, as a function of the LiOH concentration of the mineralizer solution.

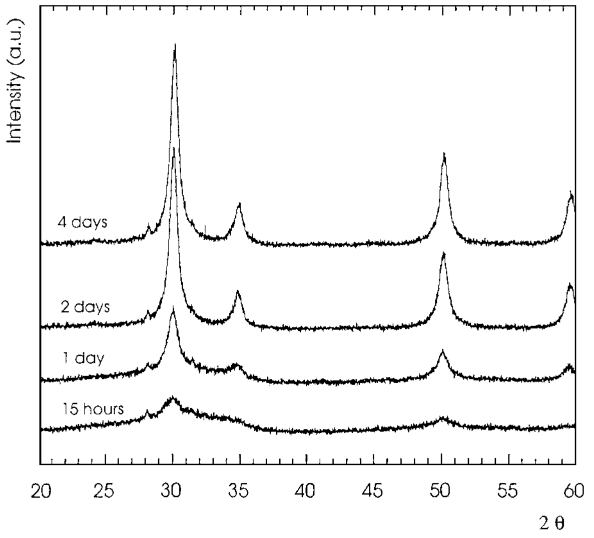

Figure 6 XRD powder patterns of products obtained by hydrothermal treatment at 110°C and in presence of 0.25 M NaOH solution for ZrO_2-17 mol% CaO as a function of the reaction time.

3.2.4. Effective stabilization of hydrothermally synthesized ZrO_2-CaO solid-solutions

In order to ascertain the true stabilization of the so prepared CSZ samples, they were annealed in air for 6 hours between 600 and 1300°C. The high surface area of such powders and as a consequent an excess surface energy might determine the formation of metastable phases of undoped zirconia [29]. A thermal treatment of metastable phases at increasing temperatures, determines a diminution in the surface energy of powders due to their grain growth with consequent transformation into stable phases of zirconia. In our case, an increase of the crystal sizes for the hydrothermally synthesized phases has been observed at increasing temperatures of thermal treatment, nevertheless no polymorphic transformations were involved. However, a certain portion of monoclinic or tetragonal ZrO_2 was produced after thermal treatment of partially crystallized powders. This behaviour is to be related the following thermal evolution in air of the uncrystallized portion of ZrO_2:

$$\text{Amorphous } ZrO_2 \xrightarrow{430\,^\circ C} \text{Tetragonal } ZrO_2 \xrightarrow{>600\,^\circ C} \text{Monoclinic } ZrO_2$$

The thermal crystallization of amorphous ZrO_2 into the tetragonal form may be in advance foreseen in DTA curve through the presence of the typical exothermic peak at 430°C due to the portion of uncrystallized ZrO_2 in the products.

The anomalous cubic phases produced with CaO content higher than 20 mol%, when heated at temperature higher than 1000°C, transform in well crystallized cubic samples plus $CaZrO_3$ according to the binary system [26]. This behaviour shows that the phase relations are different for doped zirconia synthesized by hydrothermal treatment respect to analogous samples obtained through solid state reaction. However, at high temperature the ternary ZrO_2-CaO-H_2O system becomes equivalent to that of binary ZrO_2-CaO system.

4. Conclusions

The hydrothermal treatment performed on the ZrO_2-CaO-M_2O ($M = $ Na, Li) system allows to synthesize ZrO_2-CaO solid solutions with a wide range of composition and different crystallinity. Taking the composition of zirconia-based phase constant, the crystal sizes can be changed widely by the hydrothermal process temperature as well as the concentration of mineralizer solution. The presence of the alkaline hydroxide in the starting mixtures of precursors appears fundamental to the crystallization-stabilization of zirconia at very low process temperature. A high pH value of the mineralizer solution favours the structural rearrangement of zirconia gel during the crystallization. The strong base MOH promotes, in fact, the formation of oxo-bridgings between non-bridgings hydroxyl groups of gel [30] so influencing the nucleation rate and, consequently, the crystal growth. Taking the conditions of hydrothermal treatment constant, an increasing alkalinity of the mineralizer solution promotes the formation of products characterized by a decreasing surface area. Such behaviour explains, in terms of surface-energy theory, the progressive occurrence of monoclinic, tetragonal and cubic zirconia.

About the role of CaO in the stabilization of zirconia, it must be into account the relatively low solubility of $Ca(OH)_2$ ($K_{ps} = 4 \times 10^{-5}$). In this case, the corresponding and low OH^- concentration involves an insufficient structural rearrangement of gel which avoids its crystallization as experimentally observed in performing the hydrothermal treatment in presence of only CaO. With the addition of MOH mineralizer, nevertheless the decreased Ca^{2+} concentration, due to the effect of common ion, the structural rearrangement of gel was so high as to give the crystallization-stabilization of zirconia.

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