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Zirconia-yttria (8 mol%) powders hydrothermally synthesized from different Y-based precursors

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Abstract

Nanometric powders of yttria (8 mol%) stabilized cubic zirconia were hydrothermally synthesized from amorphous zirconia at 110 °C for 7 days in the presence of ($KOH + K_2CO_3$) mineralizer solutions at different concentrations. Different Y-based precursors were employed in mixtures with zirconia xerogel: crystalline $Y(OH)_3$, crystalline Y_2O_3 and $Y(OH)_3$ xerogel as a Zr–Y coprecipitate. The type of Y-based precursor and the concentration of the mineralizer noticeably affect the characteristics of cubic ZrO_2 crystallized as the main phase. The resulting powders differ, in fact, in terms of reactivity, degree of agglomeration, amount of both monoclinic ZrO_2 and uncrystallized zirconia. Regarding the sinterability of the various powders, poor defects YSZ-based ceramics were produced from powders characterized by crystallites relatively larger in size. Such characteristics are typical of the powder hydrothermally synthesized from the mechanical mixture of crystalline Y_2O_3 and zirconia xerogel in the presence of dilute solution of the mineralizer.

Keywords: Fuel cells; Grain size; Hydrothermal synthesis; Ionic conductivity; ZrO_2

1. Introduction

Yttria-stabilized cubic zirconia is one of the most investigated ceramic materials because it is widely used as a solid electrolyte in high-temperature electrochemical devices.[1,2]

To produce high quality yttria-stabilized zirconia ceramics, it is necessary to dispose of powdered precursors with high purity, nanometer-sized primary particles, narrow sizes distribution and weakly bonded primary particles. To this end the hydrothermal treatment al low temperature appears an inexpensive and simple method of synthesis.[3–5]

In this study the characteristics of zirconia-yttria (8 mol%) powders synthesized from different yttria precursor and in the presence of mineralizer solution at different concentration will be presented.

2. Experimental

ZrO_2 xerogel was obtained by adding a $ZrCl_4$ solution to ammonia (~4 M). The corresponding precipitate was filtered, repeatedly washed with distilled water until no reaction for Cl ions (with $AgNO_3$ 1 M) was observed, and finally dried at 60 °C overnight. The yttria-based precursors were: crystalline $Y(OH)_3$, crystalline Y_2O_3 and $Y(OH)_3$ xerogel obtained as a Zr–Y coprecipitate. The last one was obtained by adding a $ZrCl_4$–$Y(NO_3)_3$ dilute solution to ammonia (~4 M). The mineralizer solutions were prepared with K_2CO_3 and KOH. Taking the K_2CO_3/KOH molar ratio constant and equal to 3, the total ($K_2CO_3 + KOH$) concentration was changed between 0.05 and 2.0 M.

Hydrothermal syntheses were performed at 110 °C for 7 days. All of the precursors contained 8 mol% Y_2O_3. ZrO_2 xerogel was mechanically mixed with crystalline Y_2O_3 or with crystalline $Y(OH)_3$ whereas $Y(OH)_3$ xerogel was employed as a coprecipitated (Zr,Y) hydroxide xerogel.

The synthesized powders were characterized by XRD and DTA–TG. The average crystal sizes were calculated

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by the Scherrer formula, with the Warren correction and calibration with polycrystalline silicon, by measuring the half-width of the XRD $(111)_C$ diffraction peak. The crystalline content of *c*-zirconia was determined by adopting the intensity relationship:

$$\frac{I(111)_C}{I(111)_C+I(\bar{1}11)_M+I(111)_M}$$

The powders were compacted in cylindrical pellets by cold isostatic pressing at 150 MPa and sintered at 1500 °C for 2 h.

The microstructures were revealed with SEM observations after thermal etching at 1300 °C for 1 h.

3. Results and discussion

The powders hydrothermally synthesized in the presence of crystalline yttria based precursors, resulted mainly in *c*-zirconia and a small amount of *m*-ZrO_2, whereas only *c*-zirconia crystallized from the Zr–Y coprecipitate (Fig. 1). It is noteworthy to observe that in the range (0.20–0.50 M) of dilute mineralizer solutions, full crystallization occurred, as confirmed by the absence of typical DTA exothermic peak at about 420 °C, due to the crystallization of uncrystallized fraction of zirconia. Furthermore, the powders synthesized in the dilute mineralizer solutions are characterized by bigger crystallite sizes than ones synthesized in the presence of concentrated solutions (Table 1).

To explain these results, both the crystallization rate of zirconia xerogel and its stabilization rate must be considered.[6] The stabilization involves an interaction between a soluble Y-containing species in the mineralizer solution and the crystallizing zirconia. The $Y(OH)_3$ xerogel precursor is characterized by the highest reactivity, intermediate solubility and homogeneous dispersion in the Zr–Y coprecipitate. All of these features favour the full stabilization of zirconia in the cubic polymorph. In the presence of less reactive or less soluble Y_2O_3-based precursors,[7,8] i.e. crystalline Y_2O_3 or $Y(OH)_3$, respectively, an incomplete stabilization of zirconia resulted as confirmed by the presence of a certain *m*-ZrO_2 fraction. Smaller crystallite sizes resulted for

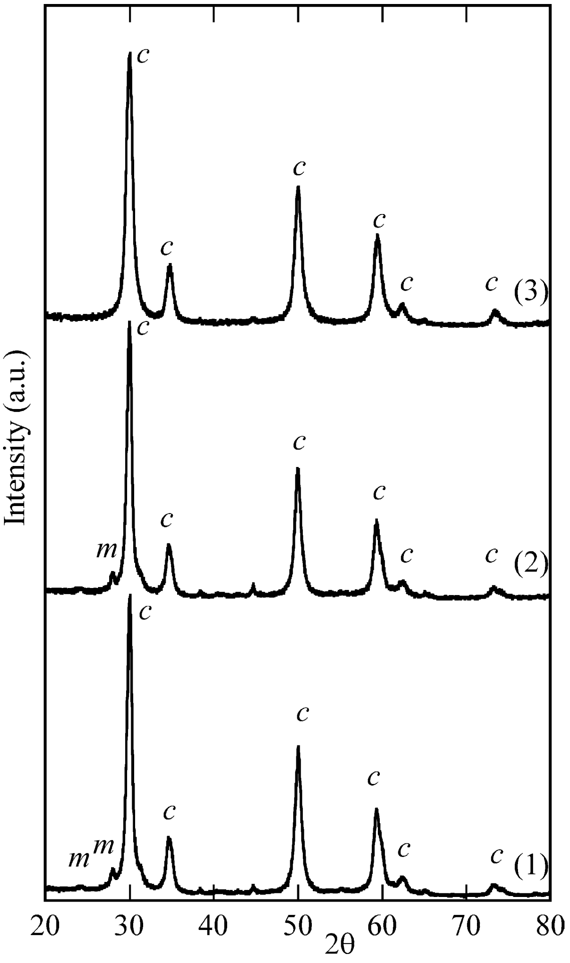

Fig. 1. XRD patterns of powders hydrothermally synthesized in the presence of 0.20 M mineralizer solution and with different Y_2O_3-based precursor: crystalline Y_2O_3 (1), crystalline $Y(OH)_3$ (2) and $Y(OH)_3$ xerogel of the Zr–Y coprecipitate (3). *c* = Cubic zirconia, *m* = monoclinic zirconia.

Table 1
Characteristic of as-synthesized powders and after calcination at 900 °C for 5 min

Y_2O_3-based precursor	Molarity of mineralizer solution	*c*-Zirconia content (%)	Crystal size (nm) of *c*-zirconia	Uncrystallized zirconia content	*c*-Zirconia content (%) after calcination at 900 °C	Crystal size (nm) of *c*-zirconia after calcination at 900 °C
Crystalline Y_2O_3	0.05 M	81[c]	13.7	**[b]	95	15.1
Crystalline Y_2O_3	0.20 M	79	18.9	–	95	19.1
Crystalline Y_2O_3	1.0 M	89[c]	16.8	*[a]	96	19.7
Crystalline Y_2O_3	2.0 M	90[c]	13.4	*[a]	97	18.8
Crystalline $Y(OH)_3$	0.20 M	91	16.7	–	96	19.7
Crystalline $Y(OH)_3$	2.0 M	94[c]	12.8	*[a]	100	17.7
$Y(OH)_3$ xerogel	0.20 M	100	11.8	–	100	15.1
$Y(OH)_3$ xerogel	2.0 M	100[c]	8.3	*[a]	100	17.4

[a] *Traces content of uncrystallized zirconia.

[b] **Low content of uncrystallized zirconia.

[c] Respect to the crystalline phases.

powders synthesized in the presence of the concentrated mineralizer solutions. The crystal sizes of c-ZrO_2 are affected, in fact, by the nucleation rate, which is in turn proportional to the mineralizer concentration. Thus, the higher the mineralizer concentration the higher the nucleation rate and then smaller particle sizes result.

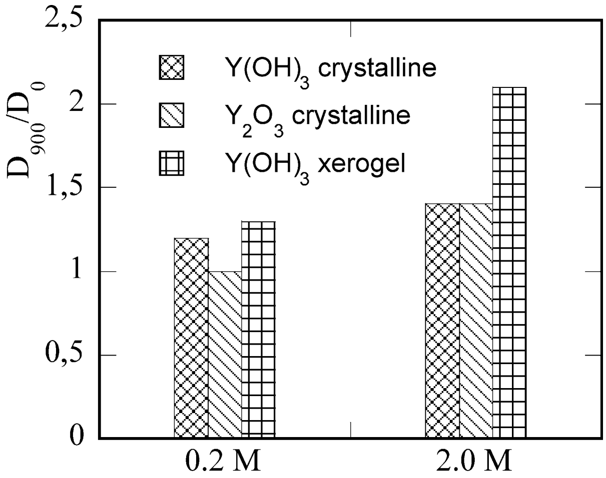

Fig. 2. D_{900}/D_0 ratio of c-zirconia of powders synthesized from different Y-based precursors in the presence of dilute (0.20 M) and concentrated (2.0 M) mineralizer solutions. D_{900} = average crystal size of c-zirconia after calcination at 900 °C for 5 min; D_0 = average crystal size of c-zirconia of the corresponding as-synthesized powders.

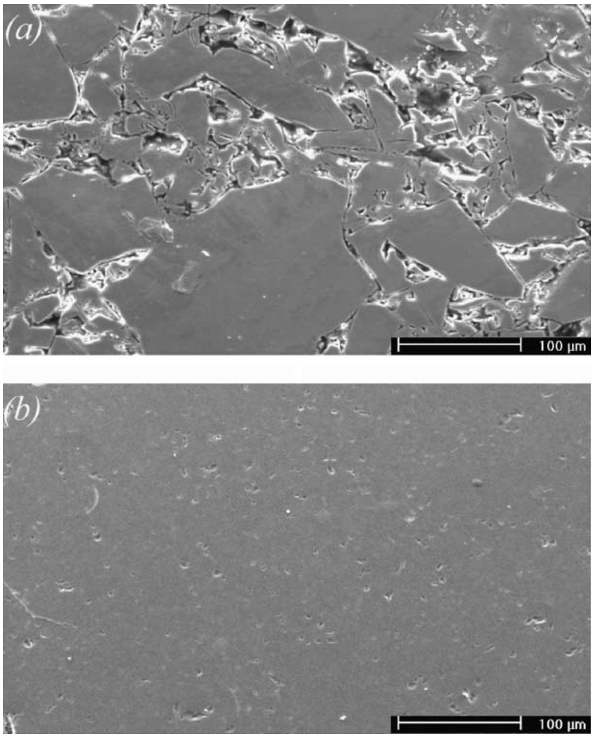

Fig. 3. SEM micrographs of two samples sintered at 1500 °C for 2 h. Sample (a) obtained from Zr–Y coprecipitated precursor in the presence of 0.2 M; Sample (b) obtained from crystalline Y_2O_3 and ZrO_2 xerogel mixture in the presence of 0.2 M of mineralizer solution.

The different reactivity of the as-synthesized powders appears readily after a calcination step at 900 °C for 5 min. The most reactive powders, obtained from the coprecipitates and in the presence of the concentrated mineralizer solution, showed a noticeable coarsening pointed out from the D_{900}/D_0 ratio, where D_{900} is the average crystal size after the calcination step at 900 °C and D_0 is that one of the corresponding as-synthesized powders (Fig. 2).

The microstructure of sintered compacts, previously calcined at 900 °C, resulted very different, depending on both the type of Y_2O_3-based precursor and concentration of mineralizer. A very poor densification on sintering at 1500 °C for calcined powders characterized by a high coarsening resulted. The sintered sample obtained from Zr–Y coprecipitate and in the presence of dilute mineralizer solution, shows, in fact, a poor densification (Fig. 3a); on the contrary, well densified products resulted for samples obtained from crystalline Y_2O_3-based precursor and in the presence of dilute mineralizer solution (Fig. 3b).

4. Conclusion

Zirconia xerogel hydrothermally treated with different Y_2O_3-based precursors (8 mol% as Y_2O_3), and in the presence of ($K_2CO_3 + KOH$) mineralizer at different concentrations, enable the crystallization-stabilization of c-zirconia as the main phase, with possibly monoclinic phase. The synthesized powders differ in reactivity, degree of agglomeration and m-ZrO_2 content. Of course the best performances on sintering are achieved using powders with the lowest coarsening on calcination. Such powders are obtained in dilute mineralizer solution and in the presence of crystalline Y_2O_3 as yttria precursor.

Acknowledgements

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