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Preparation of nanosized yttria-stabilized zirconia powders and their characterization

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Yttria-stabilized zirconia (YSZ) powders have been prepared by basic hydrolysis of a solution containing zirconium isopropoxide and yttrium nitrate. Crystallization of cubic YSZ occurs near 450 °C yielding ceramic powders with high specific areas, the values of which are dependent on the ammonia and water contents of the hydrolysis solution. Sintering at 1420 °C yields ceramics with nearly theoretical density and homogeneous grain size distribution.

1. Introduction

Zirconia, ZrO_2, is a well-known material that exhibits three structural modifications: monoclinic up to 1170 °C, tetragonal up to 2370 °C, and cubic. The fluorite-like cubic modification can be stabilized by a variety of oxide additions, one of which is yttria (Y_2O_3). Yttria-stabilized zirconia (YSZ) has been used as a crucible material, as a jewel stone and as a solid electrolyte. In this last case, applications like batteries, fuel cells, oxygen probes and sensors have been developed. Sintering of pure stabilized zirconia needs high firing temperatures yielding excessive grain growth. Use of grain growth inhibitors such as SiO_2, Al_2O_3 or TiO_2 [1–3] or of very effective sintering promotors such as Bi_2O_3 [4, 5] have been proposed in order to increase the ceramic properties. Another way concerns the elaboration of very reactive and fine particles. Such a method implies a chemical process and hydrolysis of metal alkoxides has been successfully developed [6, 7]. In both cases, zirconium and yttrium alkoxides are dissolved in a mutual organic solvent (*n*-hexane or benzene) and hydrolysis is performed by dropwise addition of water into the solution under vigorous stirring. After drying and calcination, very fine-grained powders are obtained exhibiting low-temperature sinterability (1180 to 1330 °C) and leading to improved YSZ ceramics [7–10].

We have explored [11] similar routes to YSZ ceramic powders and it has appeared that the sol–gel process yields better results than metallo-organic decomposition (MOD). This paper focuses on the production and characterizations of YSZ powders obtained by hydrolysis of zirconium alkoxide, yttria being introduced as a mineral salt.

2. Experimental procedure

2.1. Starting solutions

2.1.1. *Mixture solution of $Y(NO_3)_3$ and $ZrO(OC_3H)_4$ in isopropanol*

$Y(NO_3)_3{\cdot}6H_2O$ was dissolved in isopropanol under stirring for around 15 min at room temperature yielding a clear solution with a 5 wt % concentration in yttrium. $Zr(OC_3H_7)_4$ was added into the previous solution according to the stoichiometry of a final composition of $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ after calcination. At the beginning, $Zr(OC_3H_7)_4$ settled at the bottom of the beaker. After 20 to 30 min stirring, a homogeneous and clear solution of pH 3 to 4 was obtained (Solution I).

2.1.2. *Hydrolysis agent*

Ammonia solution (30 wt % NH_3) dissolved in isopropanol was used as the hydrolysis agent. In order to follow the influence of the H_2O/Zr ratio on the process, different solutions were prepared with H_2O/Zr ranging from 1/1 to 20/1, the water quantity being adjusted by further addition of pure water into the alcoholic solution (Solution II).

2.2. Hydrolysis and gelation

Hydrolysis was carried out by pouring Solution I into II or vice versa under vigorous stirring. According to the ammonia and water contents of the hydrolysis solution, either sol, gel or precipitate can be obtained. The results are summarized in Table I.

2.3. Drying

Drying was performed at about 110 °C in a heating desiccator overnight. The dried products were not transparent. When a precipitate was formed, the uplayer liquid was removed before drying.

3. Characterizations

3.1. Thermal analysis

Differential thermal analysis (DTA) was carried out between room temperature and about 950 °C. All dried samples exhibited almost the same DTA curves,

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TABLE I Hydrolysis results

Sample	NH_3/PrOH	H_2O/Zr	OH^-/NO_3^-	Mixing-method	Results
1	5%	1	0.85	II → I	Monolithic gel, taking 5 min
2	10%	4	3.5	II → I	A soft gel with liquid
3	10%	4	3.5	I → II	From gel change in sol
4	10%	10	3.5	I → II	Precipitate
5	10%	20	3.5	I → II	Precipitate
6	20%	1	2	I → II	Precipitate
7	20%	5/2	2	I → II	Precipitate

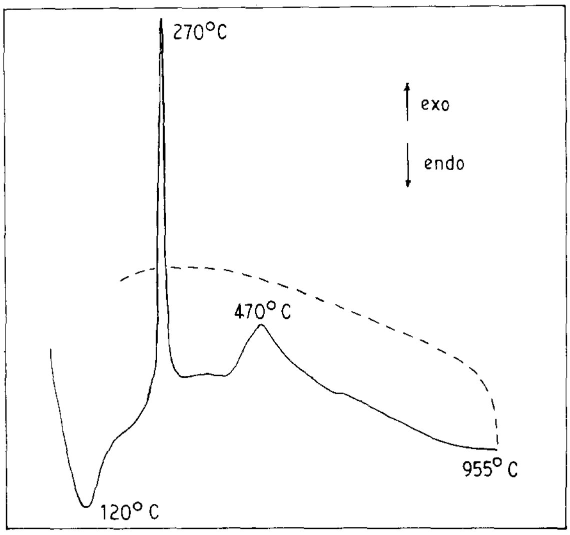

Figure 1 Typical DTA curve for a gel dried at 110 °C (sample 1).

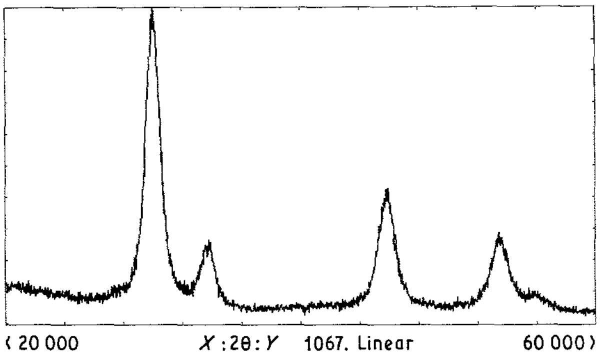

Figure 2 X-ray diffraction pattern of sample 4 after 500 °C calcination.

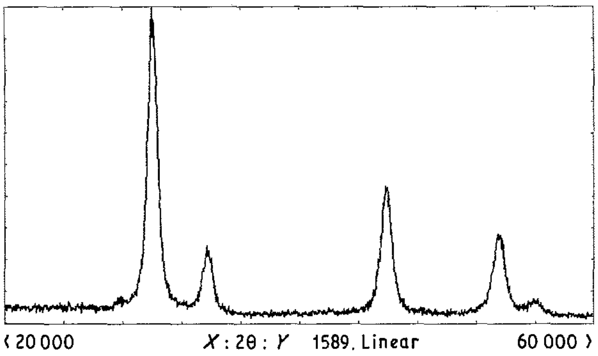

Figure 3 X-ray diffraction pattern of sample 4 after 700 °C calcination.

one of these is shown in Fig. 1. There is an endothermic peak at about 120 °C, which may correspond to the evaporation of the residual water and organic solvent. A rather strong exothermic peak appears around 250 °C and can be attributed to the burning of organic groups and the formation of the amorphous zirconia. Probably due to the transition from amorphous zirconia into the cubic phase, a rather wide exothermic peak is observed around 440 °C. No other thermal effect was observed up to 950 °C. When cooling down, neither endo- nor exothermic peaks were observed. The results may indicate that the phase formed at about 450 °C is stable. No relation clearly appears between the production conditions (mixing method, H_2O/Zr ratio, etc.) and the temperatures of the thermal effects. Only sample 1 revealed a small difference compared to the other ones, the crystallization effect appearing at 470 °C instead of 440 ± 4 °C as a mean value for samples 2 to 7.

The dried samples were calcined at 400, 500 and 700 °C. In all cases, the heating rate was 250 °C h^{-1} and the samples were kept at the corresponding temperature for 4 h, and finally furnace cooled to room temperature.

3.2. X-ray diffraction measurements

After 400 °C calcination, all samples appeared to be amorphous by X-ray diffraction. Figs 2 and 3 show X-ray diffraction patterns for the powders calcined at 500 and 700 °C, respectively. Obviously the cubic phase of Y_2O_3 stabilized ZrO_2 (YSZ) is formed at 500 °C without any monoclinic or free Y_2O_3 phase. The powders obtained by calcining at 700 °C show nearly the same diffraction patterns as at 500 °C, except that the diffraction peaks become narrower. However, no new phase was observed, indicating that Y_2O_3 has been perfectly dissolved into the ZrO_2 lattice to form a solid solution. Refinement of the cell parameter from the diffraction data yields a_0 mean values of 0.5154(5) and 0.5152(4) nm for 500 and 700 °C calcinations, respectively. These values are slightly higher than that expected for the composition $92ZrO_2 \cdot 8Y_2O_3$, 0.5139 nm [12]. However, the width of the diffraction lines can explain the observed discrepancies.

3.3. Specific area measurements

Specific areas of the calcined powders have been measured by means of single-point BET technique. The results are listed in Table II. It is obvious from

TABLE II BET specific area

Sample no.	Specific area ($m^2 g^{-1}$)	
	500 °C[a]	700 °C[a]
1	86	47
2	100	75
3	102	79
4	120	96
5	116	95
6	114	94
7	115	94

[a] Calcination temperature.

Table II that the specific areas of powders calcined at 500 °C are bigger than those calcined at 700 °C. The mixing method for Solutions I and II does not affect the specific area, as comparing sample 2 with sample 3 shows that increasing the H_2O/Zr ratio from 1 to 4 by means of higher ammonia concentration, yields an increase in the corresponding specific areas from 47 to 75 $m^2 g^{-1}$ after 700 °C calcination. Further increase of the H_2O/Zr ratio to 10 allows the highest values, around 96 $m^2 g^{-1}$, to be obtained. If the H_2O/Zr ratio reaches 20, no further modification of the specific area is observed.

3.4. SEM observation of powders

Fig. 4 shows the morphologies of powders calcined at 700 °C. Most of them occur as aggregates, which are not easily dispersed even by ultrasonic vibration for several minutes. A decrease in the mean particle size from 0.5 to 1 µm to around 100 nm for samples 1 and 3, respectively, is observed. The other samples exhibit particle sizes below 100 nm. These results follow the same sequence as the evolution of the BET specific areas.

3.5. Sintering and phase composition of ceramics

Powder samples were pressed into pellets using a steel die with 7 mm diameter under a pressure of 2 ton cm^{-2}.

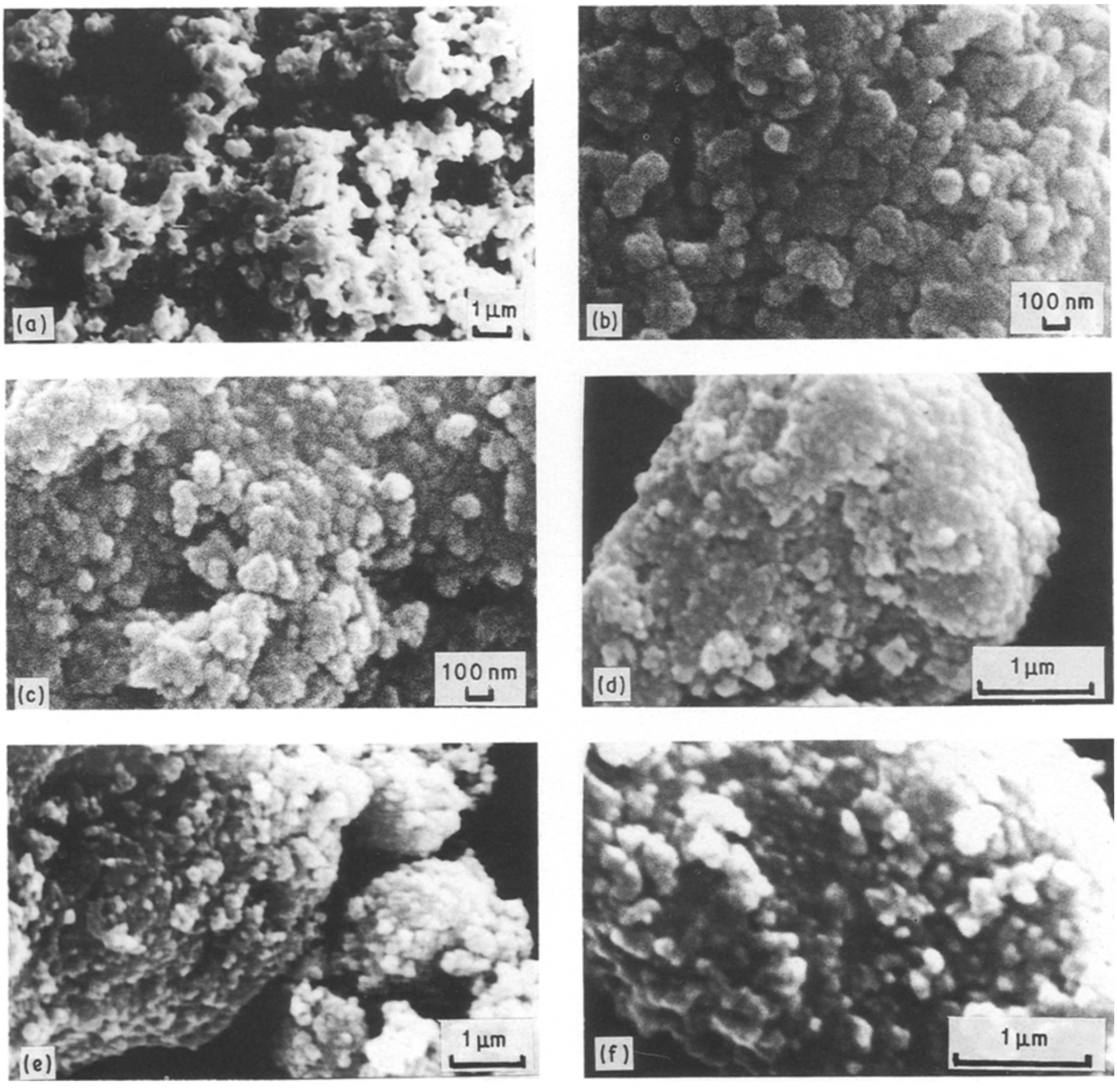

Figure 4 Scanning electron micrographs of powders calcined at 700 °C for 4 h. Samples: (a) 1, (b) 3, (c) 4, (d) 5, (e) 6, (f) 7.

Sintering was carried out in a zirconia crucible under air atmosphere at 1420 °C. The sintering schedule was as follows: the samples were heated at 200 °C h^{-1} and sintered at 1420 °C for 8 h. Then they were furnace cooled to room temperature. The densities of the sintered samples were measured by the immersion method; the measured densities are listed in Table III. It can be observed that the densities of sintered YSZ ceramics increase with increasing specific area of the powder. A mean density of about 5.94 g cm^{-3} can be obtained for the powders with a specific area around 100 m^2 g^{-1} (samples 4 to 7). Therefore, ceramics with a final density very close to the theoretical one (better than 99%) can easily be achieved by sintering at 1420 °C, a temperature which already appears attractive for sintering of yttria-stabilized zirconia.

The X-ray diffraction patterns reveal a pure yttria-stabilized zirconia phase with the cubic structure (Fig. 5 for sample 4). Refinement of the cell parameter yields a value of 0.514 0(1) nm, very close to the expected one [12]. No impurity phase was observed. Very narrow peaks may indicate that the crystallites are well developed. (The background fluctuations are due to the amorphous sample holder.)

TABLE III Densities of sintered samples from powders calcined at 700 °C

Sample no.	Mean density (g cm^{-3})	Specific area (m^2 g^{-1})
1	5.43	47
3	5.60	79
4	5.95	36
6	5.94	94

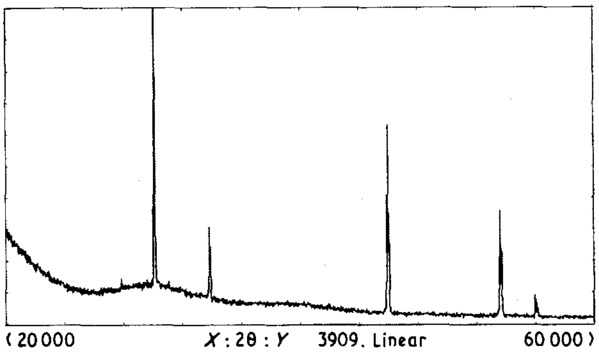

Figure 5 X-ray diffraction pattern of a ceramics sintered at 1420 °C (sample 4).

3.6. Microstructures of sintered YSZ ceramics

Fig. 6 shows the scanning electron micrographs of the natural surface of sintered samples 3, 5, 6 and 7. The microstructural features are dense and without any microfissure. The grain size is essentially uniform and ranging from 1 to 4 μm. Compared to samples 5, 6 and 7, a few more pores are observed on sample 3, in agreement with its lower density. These pores are located either inside the grains or at the grain boundaries.

4. Conclusion

YSZ powders exhibiting a high sinterability around 1400 °C can be obtained by hydrolysis of $Zr(OC_3H_7)_4$–$Y(NO_3)_3$ solution in isopropanol by means of ammonia. The hydrolysis product can be converted into Y_2O_3-stabilized ZrO_2 with a pure cubic structure after calcination above 500 °C. The

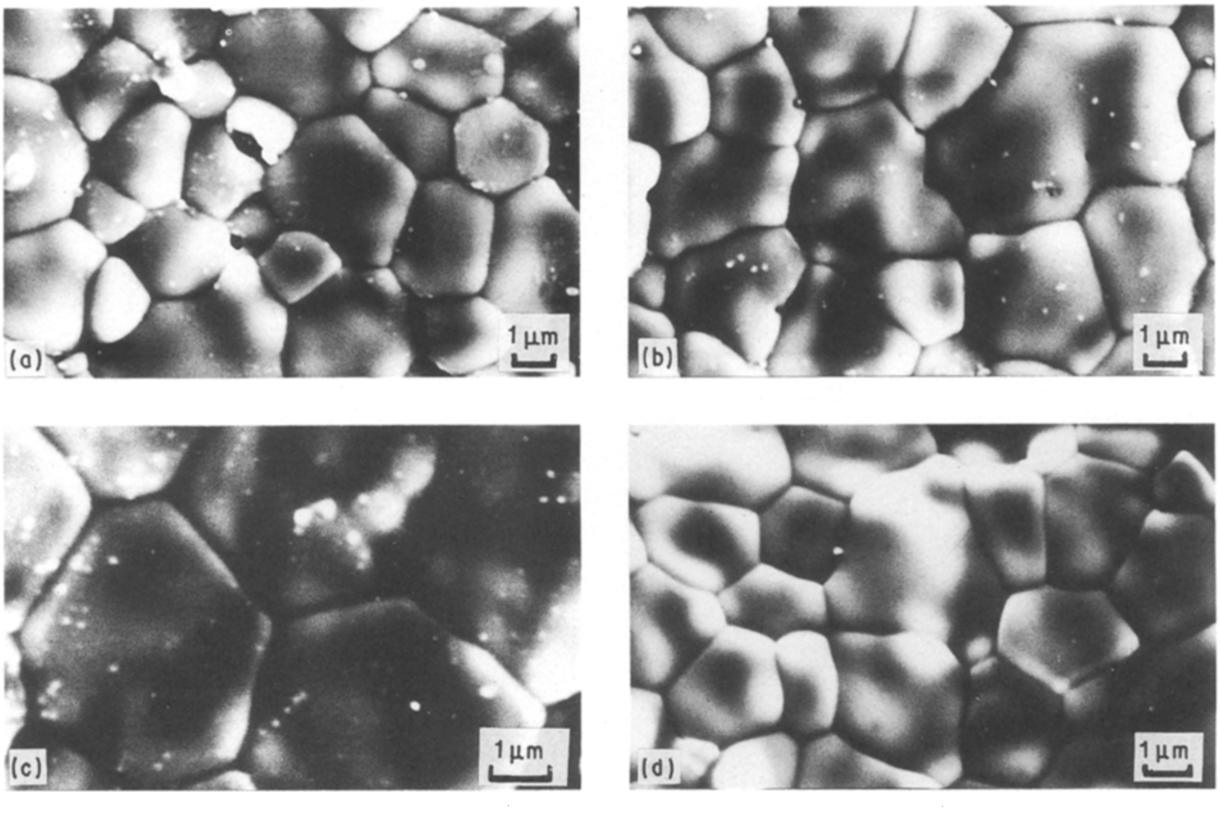

Figure 6 Scanning electron micrographs of the natural surface of sintered YSZ samples. Samples: (a) 3, (b) 5, (c) 6, (d) 7.

observed specific areas are related to the ammonia and water amounts. Values around 100 and 120 $m^2 g^{-1}$ for calcinations at 700 or 500 °C, respectively, can be obtained when the ratio OH^-/NO_3^- equals 1 and the ratio of H_2O/Zr equals roughly 10. Further increase of the ammonia and water amounts has no further influence on the specific area. The particle sizes of YSZ powders with a specific area of 100 $m^2 g^{-1}$ are pretty uniform and smaller than 100 nm. The powders can be sintered at a temperature of 1420 °C yielding a final density better than 99% theoretical. The sintered YSZ ceramics reveal a pure cubic phase and a microstructure with dense matrix and fine grain size below 4 μm. It may be expected that powders with much better sinterability and finer YSZ ceramics could be obtained by calcination at temperatures between 500 and 700 °C and by carefully handling the preparation process. This technique may also be used for zirconia ceramics stabilized by other rare-earth oxides.

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