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Microwave-Hydrothermal Synthesis of Nanocrystalline Zirconia Powders

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Nanosized zirconium oxide (ZrO_2) powders were prepared by adding NaOH to a zirconyl chloride aqueous solution under microwave-hydrothermal conditions. The obtained results showed that the tetragonal polymorph increased with increasing NaOH concentration in the starting solution and reached the maximum value by using 1*M* $ZrOCl_2$. The microwave-assisted hydrothermal synthesis is expected to be able to process continuously, and may lead to energy savings because of rapid heating to temperature and increased kinetics of crystallization. This method is very simple and can lead to powders with desirable characteristics such as very fine size, narrow size distribution, and good chemical homogeneity.

I. Introduction

OVER the years, zirconium oxide (ZrO_2) ceramics have been largely used because of their chemical and physical properties, such as excellent chemical resistance, high refractoriness, and ionic conductivity.

To achieve such desirable properties, the synthesis conditions must be well-controlled to obtain fine powders with a narrow particle size distribution that enhance reactivity and densification. Among the various methods, hydrothermal crystallization[1–3] is an interesting process used to directly prepare submicrometer- and nanometer-sized crystalline powders with reduced contamination and low synthesis temperature. A recent innovation to the hydrothermal method, developed by Komarneni *et al.*,[4–6] involves the introduction of microwaves during the hydrothermal synthesis to increase the kinetics of crystallization by 1–2 orders of magnitude.

The purpose of the present work is to report the synthesis of ultrafine ZrO_2 powders under microwave-assisted hydrothermal conditions. The effects of various synthesis parameters, such as solution pH, concentration of ions, temperature, and reaction time on powder properties, such as the type of polymorph, crystallite size, particle size distribution, and degree of agglomeration, were investigated.

II. Experimental Procedure

(1) Sample Preparation

The microwave-assisted hydrothermal synthesis of ZrO_2 powders was conducted using various concentrations (from 0.5*M* to 10*M*) of $ZrOCl_2 \cdot 8H_2O$ aqueous solutions. The solutions were neutralized with NaOH (from 0.5*M* to 1*M*) to pH 9. The mixture was then treated in a Teflon-lined vessel using a microwave digestion system (Model MDS-2000, CEM Corp., Matthews, NC). This system uses 2.45 GHz microwaves and is controlled by pressure. It can attain a maximum pressure of 200 psi, which is equivalent to ~194°C, based on steam tables. The reaction vessel was connected to a pressure transducer that monitors and controls the pressure during synthesis.

After preliminary tests, microwave-hydrothermal treatments were conducted at 200 psi for 2 h. The time, pressure, and power were computer controlled. After the synthesis reaction, the powder was filtered, washed, and dried. After the last washing of the synthesized powder, the supernatant was analyzed by ICP spectroscopy (Model Liberty 200, Variant, Sidney, Australia) to evaluate the presence of sodium and the efficacy of the washing step.

(2) Powder Characterization

All the synthesized products were analyzed with a computer assisted X-ray (CuKα) powder diffractometer (Model PW3710, Philips Research Laboratories, Eindhoven, The Netherlands). The XRD patterns were collected in a 2θ range of 25°–90° at room temperature, with a scanning rate of 0.005°/s and a step size of 0.02°. Lattice parameters of monoclinic, $[P2_{1/a}]$,[7] and tetragonal, $[P4_{2/nmc}]$,[8] phases were determined by a least-squares refinement and the average grain size by using the Sherrer's formula.[9] A quantitative determination of the volume fraction in the mixture of both monoclinic and tetragonal phases was made by using the following formula:[10]

$$X_t = \frac{I(111)_t}{I(\bar{1}11)_m + I(111)_m + I(111)_m} \quad (1)$$

where the subscripts m and t refer to the monoclinic and tetragonal phases and I refers to the X-ray intensity of the corresponding peaks. The sample morphology was examined by TEM (Model EM400, Philips Research Laboratories). The surface area analysis was conducted on the powders by BET (Model Gemini 2360, Micromeritics Instrument Corp., Norcross, GA), using nitrogen as an adsorbate. The particle size was also calculated, using the specific surface area data, by the equation:

$$\phi = \frac{6}{S\rho} \quad (2)$$

where ϕ is the average diameter of a spherical particle, S is the surface area of a powder, and ρ is the experimental density value of powder measured by a helium picnometer (Model Accupic 1330, Micromeritics Instrument Corp.). Finally, the thermal stability of the powders was evaluated by DTA (Model 404, Netzsch, Selb, Germany).

III. Results

The as-prepared powders contained only ZrO_2 as a crystalline phase whose crystal symmetry varied with synthesis conditions.

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Table I. Lattice Parameters of ZrO_2 Powders Obtained by Different Synthesis Conditions

Sample	Monoclinic ZrO_2				t′-ZrO_2		
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	c (Å)	c/a
Zr1Na0.5	5.324(13)	5.203(11)	5.153(14)	99.59(14)	5.118(8)	5.192(6)	1.015
Zr1Na1	5.287(15)	5.208(15)	5.119(15)	99.42(19)	5.118(8)	5.183(8)	1.013
Zr1Na10	5.319(6)	5.198(6)	5.142(5)	99.50(5)	5.116(8)	5.196(7)	1.016
Zr0.5Na10	5.325(7)	5.202(6)	5.143(4)	99.62(5)	5.130(8)	5.209(8)	1.016
Zr0.05Na1	5.322(7)	5.199(7)	5.137(5)	99.66(5)			
Zr0.5Na1	5.317(5)	5.194(5)	5.138(3)	99.59(4)	5.130(8)	5.209(8)	1.015

The absence of alkali ions in the last washing water indicated the efficacy of the washing step. The lattice parameters of the powders obtained are given in Table I. In this case, the axial ratio is in agreement with that of the metastable t′ phase. In particular, the tetragonal polymorph increased with increasing NaOH concentrations in the starting solution (Fig. 1) and reached the maximum value by using 1*M* $ZrOCl_2$ (Fig. 2). The volume fractions of the t′ phase and the average particle size calculated by a different method are given in Table II. TEM analysis confirmed the effect of concentration on particle size. In particular, the calculated average particle size ranged from 16 (± 3) to 9 (± 3) nm, with the $ZrOCl_2$ concentration varying from 0.5*M* to 1*M*. TEM observation of particles revealed spherical-shaped particles with no agglomeration (Fig. 3), as also underlined by the small differences with the average particle size determined by X-ray line broadening. Thus, under microwave-hydrothermal conditions, the ZrO_2 powder first crystallizes in the t′-ZrO_2 phase, and then transforms into the stable monoclinic phase on further heating. From this point of view, the exothermic peak at ~400°C (Fig. 4) can be attributed to a growth phenomenon, wherein small crystals coalesce into large particles containing one or more grain boundaries.[11] As indicated by thermal analysis at ~1200°C, the monoclinic phase transformed into tetragonal. Our current study is in agreement with earlier work[12,13] on the tetragonal crystal evolution from amorphous zirconia gel materials in which topotatic crystallization on nuclei in the amorphous zirconia has been proposed as the mechanism of tetragonal zirconia formation under hydrothermal conditions.

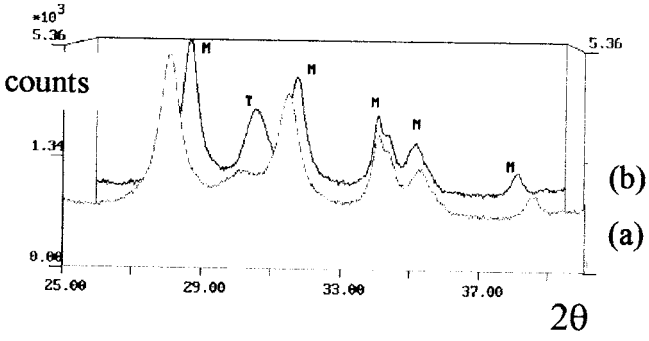

Fig. 1. XRD patterns of powders obtained starting from a (a) 0.5*M* and (b) 1*M* NaOH solution (0.5*M* $ZrOCl_2$).

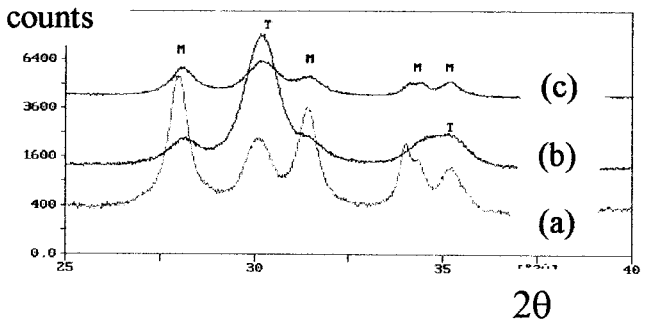

Fig. 2. XRD patterns of powders obtained starting from a (a) 0.5 *M*, (b) 1 *M*, and (c) 10*M* $ZrOCl_2$ solution (1*M* NaOH).

Table II. Volume Fractions of the t′-ZrO_2 Phase and Average Particle Size Obtained by Different Methods

Sample code	Component concentration (*M*)		Volume fraction t′ phase (%)	Grain size (nm)	
	$ZrOCl_2$	NaOH		By XRD	By BET
Zr1Na0.5	1	0.5	75.16	8.36 (t′) ND† (m)	8.45
Zr1Na1	1	1	83.36	9.5 (t′) ND† (m)	8.50
Zr1Na10	1	10	48.26	9.66 (t′) 14.76 (m)	11.31
Zr0.5Na10	0.5	10	14.89	5.78 (t′) 14.88 (m)	21.67
Zr0.05Na10	0.05	10	0	16.65 (m)	18.69
Zr0.5Na1	0.5	1	24.51	11.57 (t′) 17.42 (m)	22.92

†Cannot be accurately determined from XRD data.

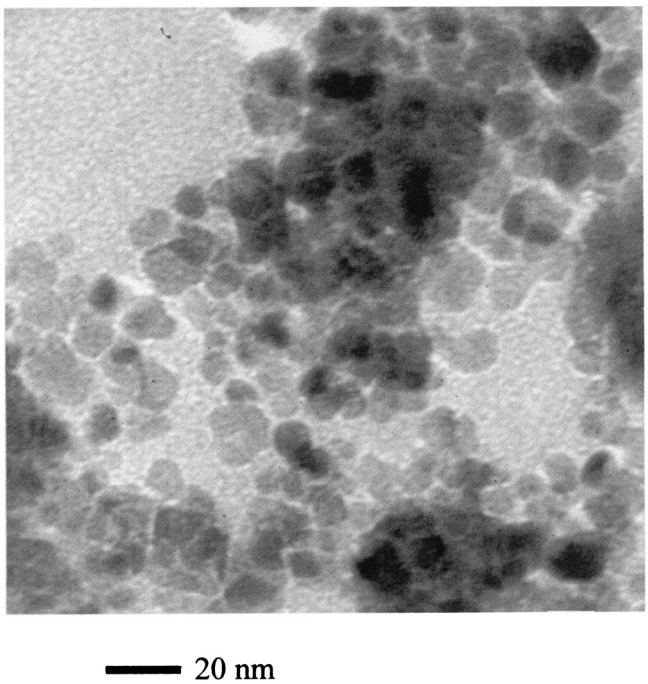

Fig. 3. TEM micrographs (130 000×) of the Zr1Na1 zirconia powders.

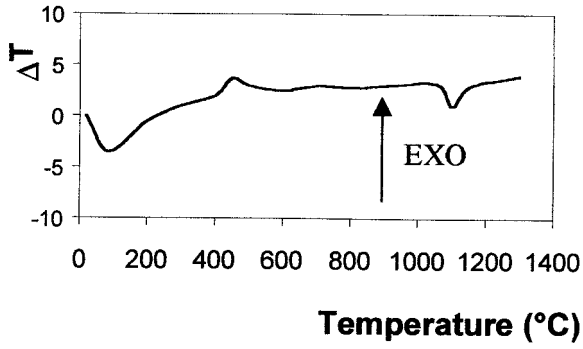

Fig. 4. DTA/TGA curves of the Zr1Na1 zirconia powder.

V. Conclusion

Nanosized and well-crystallized zirconium oxide (ZrO_2) powders were prepared by a microwave-hydrothermal method at a low temperature (200°C) using zirconyl chloride salt and NaOH as a precipitation agent. The size range of the powders was very narrow (from 10 to 20 nm) as observed by TEM and confirmed by BET and XRD results.

This study reveals that the phase stabilization process in the ZrO_2 obtained by microwave-hydrothermal synthesis has a dependence on the zirconium and NaOH concentration, and appears to be because of a critical grain size effect.[14] The powders obtained from $ZrOCl_2$ 1*M* and NaOH 1*M* had a finer particle size distribution and almost exclusively consisted of t′-ZrO_2.

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