



Investigation on the preparation and properties of monodispersed $\text{Al}_2\text{O}_3\text{--ZrO}_2$ nanopowder via Co-precipitation method



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ABSTRACT

With Al_2O_3 as inhibitor (which can be etched after calcination), monodispersed $\text{Al}_2\text{O}_3\text{--ZrO}_2$ nanopowder was successfully prepared by co-precipitation method. The as-prepared powders were characterized by acoustic particle sizer (APS), SEM, TEM and XRD, respectively. Crystalline and non-agglomerated nanometric $\text{Al}_2\text{O}_3\text{--ZrO}_2$ powders with very small crystallite size (~7 nm) and narrow size distribution can be obtained. The relative yield was affected dramatically by pH and the ratio of $M_{\text{AHC}}: M_{\text{Zr}}$. Green bodies have an ultrafine uniform microstructure without apparent macropore through 200 MPa CIP treatment. The relative density of the grains can be reached to ~98.2% by sintering at 1050 °C for 4 h, with an average grain size ~39 nm.

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1. Introduction

Due to the high reactivity, good homogeneity and sinterability, the synthesis of ceramic powders with narrow size distribution is currently of considerable interest. For example, compared to their conventional micron-crystalline counterpart, nano zirconia based ceramics has been attracted much attentions because of their good properties, superplastic behavior [1–4]. Therefore, there is a strong tendency for hard-aggregate formation during drying and calcination by liquid phase synthesis like chemical precipitation [5–8] and sol-gel processes [9]. Weakly agglomerated nanopowders can be obtained by hydrothermal synthesis. However, it is hard to control and reproduce [10,11]. Although gas phase methods are effective approaches to produce high quality agglomerate-free nanopowders, the disadvantages are involving in expensive equipment, complex operation process and requiring significant time and energy to produce relatively small amounts of material [12–15]. Co-precipitation is a process of simplicity, universality, low cost and easy to realize the industrialization if the hard-

aggregate can be avoided. Actually, hard-aggregate is consisting of many of single particles through sintering during calcination process. Typically, the addition of proper inhibitor is an effective way to suppress the process of calcination. Then, monodispersed powders can be obtained by etching the inhibitor. Till now, Al_2O_3 is often used as good inhibitor because it is inert, economic and can be easily removed.

In this study, co-precipitation technology by using Al_2O_3 as inhibitor is introduced for monodispersed $\text{Al}_2\text{O}_3\text{--ZrO}_2$ preparation. Zr^{4+} cations can be dissolved in carbonate solution forming a complex $[\text{Zr}(\text{CO}_3)_x(\text{OH})^{4-x}]^{x-}$ ($x = 0\text{--}4$, which depends on the pH) solution when addition of metal cation M ($M = \text{Ni}^{2+}, \text{Y}^{3+}, \text{Al}^{3+}$, etc) was existed to form precipitate [16]. Due to a uniform mixing in atom level of Zr and Al and formation of a kind of amorphous Al_2O_3 covered ZrO_2 structure, monodispersed $\text{Al}_2\text{O}_3\text{--ZrO}_2$ can be obtained in theory. The synthetic schematic diagram was shown in Fig. 1.

2. Experimental section

2.1. Sample preparation

Raw materials used in this experiment include $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$

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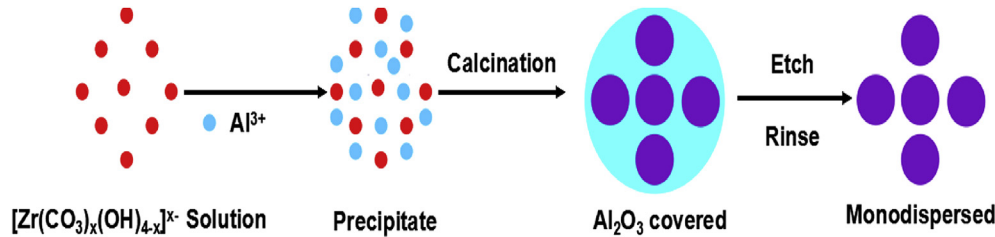


Fig. 1. Schematic diagram of preparation of monodispersed $\text{Al}_2\text{O}_3\text{-ZrO}_2$.

(analytical-reagent grade), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Kermel Chemical Reagents Co., LTD, Tianjin) and NH_4HCO_3 (AHC). The pH was adjusted by ethanediamine (2 mol/L) and nitric acid (0.2 mol/L). Nominally, 97 mol% $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $(3.5\text{--}5.0) \times 97$ mol% AHC were dissolved, respectively, and 97 mol% $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved together in deionized water. Then addition of zirconium slowly to AHC solution with a magnetic stirrer till clear solution was obtained. The final concentration of zirconium in all processes was 0.1 mol/L. Precipitates emerged when Al^{3+} mixed solution was added to zirconium complex solution dropwise. The resultant suspension was filtered and washed for four times with deionized water and three times with ethanol. After drying at 80°C overnight in air, the obtained precursors were calcined at $700\text{--}1200^\circ\text{C}$ for 2 h Fig. 2 presents a schematic flow diagram of the synthesis process.

Precursors used for yield calculation were synthesized at $\sim 1250^\circ\text{C}$ for 2 h and the obtained powder compact bodies calcined at 700°C for 10 h. The 1 and 15 mm thick samples in diameter were prepared by uniaxial pressing at 15 MPa, then calcined in air at a rate of $10^\circ\text{C}/\text{min}$ at various temperature for etching test. The concentration of NaOH corrosive liquid was 2 mol/L, and etch time and temperature were set as 2 h and 95°C , respectively. The etched bulk samples were rinsed by deionized water and dried to constant weight for weighting. The etched powder samples were rinsed by deionized water till pH reach 7.0, and ethanol washed twice times and then dried at 80°C . Putting the powders through a 60 mesh sieve, then uniaxial pressing at 4 MPa for molding and densifying

by cold isostatic pressing (CIP) at 200 MPa, after that sintered in air at a rate of $5^\circ\text{C}/\text{min}$ for sintering samples preparation (High-Temperature Furnace P330, Nabertherm, Germany). There is no need to determine the accurate etching rate of Al_2O_3 in our present experiment. Hence, the mass changes of calcined samples in etching test were determined just by analytical balance.

2.2. Samples characterization

Phase identification and average crystalline size calculation were measured by using X-ray diffractometry (XRD, X'pert PRO, PANalytical, Holland). The density of the sintered samples was calculated by the Archimedes method. The theoretical densities of the $\text{Al}_{0.12}\text{Zr}_{0.88}\text{O}_{1.94}$ crystal structure (chemical formula $\text{Al}_{0.12}\text{Zr}_{0.88}\text{O}_{1.94}$ was obtained from XRF data, not provided here) were calculated according to Eq. (1):

$$\rho_{\text{XRD}} = \frac{4 \cdot \left[x \cdot M_{\text{Y}} + y \cdot M_{\text{Al}} + (1 - x - y) \cdot M_{\text{Zr}} + \left(2 - \frac{x+y}{2} \right) \cdot M_{\text{O}} \right]}{a^3 \cdot N_{\text{Av}}} \quad (1)$$

where M is atomic weight (g/mol), x and y are the dopant mole fraction, respectively. a is the unit cell lattice parameter (\AA) and N_{Av} is Avogadro's constant. The thermal behaviors of the precursor powders were analyzed by differential scanning calorimetry (DSC)/thermogravimetry (TG) in the temperature range between 40 and 1300°C in air using a $10^\circ\text{C}/\text{min}$ ramp (DTA/TG, Netzsch 449 Thermal Analyzer, NETZSCH, Germany). Transmission electron microscopy (TEM, JEM-2010HR, JEOL, Japan) and scanning electron microscopy (FE-SEM field-emission type, XL30FEG, Philips, Holland) were used to observe the morphology and calculate size of obtained powders and bulk samples. Particle size distribution analysis of the powders was performed with acoustic particle size analyzer (APS-100, Matec Instruments Company, USA).

3. Results and discussion

3.1. Influence of pH and mole ratio on relative yield (RY)

The ratio of the ammonium bicarbonate to zirconium ($M_{\text{AHC}}: M_{\text{Zr}}$) is fixed at 4.5. The pH was adjusted slowly with nitric acid along with the addition of Al^{3+} . The RY of $\text{ZrO}_2\text{-Al}_2\text{O}_3$ significantly depends on pH, as can be seen in Fig. 3a. The RY is increasing with pH changing from 6.5 to 7.0, then decreasing (pH 7.0–8.0). Clear solution turns to turbid when pH below 7.5 or above 8.7 without Al^{3+} addition due to generation of $\text{Zr}(\text{OH})_4$. Meanwhile, flocculent precipitate emerged when Al^{3+} addition at pH excess 8.0 due to $\text{Al}(\text{OH})_3$ formation, which was detrimental to complex of $[\text{Zr}(\text{CO}_3)_x(\text{OH})^{4-x}]^{x-}$ and Al^{3+} (leading to insufficient or excessive of Al^{3+}). Fast dissolution was observed when Zr^{4+} was added to $(\text{NH}_4)_2\text{CO}_3$ and AHC mixed solution ($M_{\text{mix}}: M_{\text{Zr}} = 4.5$) at various ratio (5:1–1:5). However, less than 65% of RY was observed at all

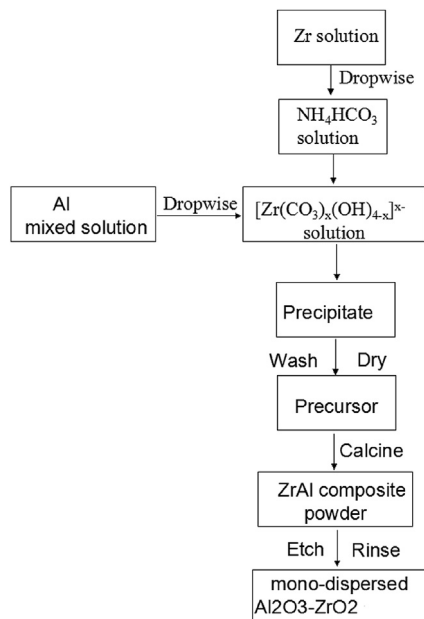


Fig. 2. A co-precipitation procedure for producing monodispersed $\text{Al}_2\text{O}_3\text{-ZrO}_2$ nanopowder.

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