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Ceramics International 36 (2010) 2231–2234
CERAMICS INTERNATIONAL
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Short communication

The preparation and characterization of soft-agglomerated ZrO_2–SiO_2 nanocrystalline composite by supercritical CO_2

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Received 12 January 2010; received in revised form 22 February 2010; accepted 16 April 2010
Available online 26 June 2010

Abstract

Zirconia–silica (50/50 vol.%) nanocomposites were prepared by supercritical CO_2 method at 15 MPa and 150 °C. The characterization of synthesized powders was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM) scanning electron microscopy (SEM) and BET. The results of XRD showed that the nanocomposite powders have mostly the tetragonal phase of zirconia (t-ZrO_2) at 1000 °C, however it was determined the tetragonal (major), monoclinic (minor) of zirconia and cristobalite (major) phases of silica were present at 1500 °C. The crystallite sizes of the t-ZrO_2 were in the range of 8–30 nm with increasing temperature from 1000 °C to 1500 °C. The surface area of samples at 1000 °C was 171 m^2/g. In addition, the agglomeration degree ($N = d^3_{BET}/d^3_{XRD}$) of powders at 1000 °C was 4, which was an indication of the soft agglomeration of powders. The stabilization of the t-ZrO_2 up to 1500 °C was attributed to the confinement of ZrO_2 particles by the surrounding cristobalite phase of silica in the structure.

Keywords: A. Powders: chemical preparation; B. Nanocomposites; D. ZrO_2; D. SiO_2

1. Introduction

Zirconia–silica composites comprise advanced physico-chemical properties such as high thermal and chemical stability, high mechanical strength and strong surface acidity [1]. Due to these advanced properties, they are considered for potential use in the application of catalytic processes, high permittivity insulating films, high fracture toughness ceramic glasses and a variety of optical coating [2–4]. It is well known that the one of the most significant problems affecting these engineering properties of nanocomposites is an agglomeration of powders during synthesis or processing. Therefore, the control of agglomeration of particles for homogenous microstructure is the most major task during the process.

Several studies can be found in the literature regarding to the synthesis of zirconia–silica composites, for instance, sol–gel, precipitation [5–7] and solid state processing [8]. Nevertheless, there is no reported experimental study of the synthesis of ZrO_2–SiO_2 nanocomposite by using supercritical fluids technology. The ceramic powders synthesized by supercritical method exhibit usually low crystallization temperature as well as better control of their particle size than conventional methods. Moreover, the surface area of the synthesized particles increase since this technique is solvent free after processing [9]. Supercritical fluids offer a convenient method for the formation of advanced nanopowders with tailored physical and chemical properties. These fluids also present a novel combination of liquid-like and gas-like physical and chemical properties, which composes these fluids unique as solvents, reaction and drying media. The properties of these fluids are continuously variable by manipulation of the pressure and temperature, which allows a tailoring of the fluid properties for applications to improve the formation of nanocrystalline powders [10,11].

Carbon dioxide, water, ammonia, alcohols and light hydrocarbons have been mostly proposed for the nanoparticles formation at supercritical conditions [12]. The supercritical CO_2 offers some advantages compared with other fluids at supercritical state. The benefits of this fluid include mild operating temperature and the facile solvent separation, recovery and recycle after process [13]. In addition, supercritical CO_2 is chemically stable, environmentally benign, non-flammable and non-toxic. Furthermore, CO_2 reaches its supercritical state at low critical temperature (31 °C) and

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0272-8842/$36.00
doi:10.1016/j.ceramint.2010.05.002

pressure (7.38 MPa) [14,15], therefore it is most widely used fluid for the synthesis of nanomaterials.

Several process for particle formation using supercritical fluids have been described in the literature. The uses of different modifications of supercritical CO_2 in material processing are related to precursor (solute) to be precipitated. When precursor is not soluble in supercritical CO_2, this method is called supercritical gas antisolvent (GAS). This method includes the dissolution of precursor in solvent that is miscible with supercritical CO_2. Then, supercritical CO_2 as antisolvent is added to the mixture of solvent and precursor, which generates supersaturation and precipitation of the solute. When the precursor is soluble in supercritical CO_2, this method is called rapid expansion of supercritical solution (RESS). In the RESS, precursor is dissolved in supercritical carbon dioxide acting as solvent at a specific range of temperature and pressure and expanded rapidly into a region of much lower pressure through a nozzle, which brings about to the decrease of its solubility and subsequent precipitation [12]. One of the most promising methods for the ceramics is a gas antisolvent method (GAS) where CO_2 are used as antisolvent to provide volumetric expansion during the particle formation subsequently forcing the solute to precipitate as particle [13–18]. In this study, a supercritical CO_2 was used to prepare ZrO_2–SiO_2 (50/50 vol.%) nanocomposite as softly agglomerated state.

2. Experimental

2.1. Chemicals

Zirconium (IV) oxynitrate hydrate (99%, Aldrich) and tetraethyl orthosilicate (98%, Fluka) were used as precursors to synthesize ZrO_2–SiO_2 (50/50 vol.%) nanopowders by the supercritical CO_2 (GAS method). Ethanol (Fluka, analytic reagent) and CO_2 were used as a solvent and an antisolvent, respectively.

2.2. Process

The supercritical synthesis was performed in a 500 ml 316 stainless steel vessel (Parr, Model 4575, 4857AEF reactor controller unit) with Teflon liner and magnetically stirring unit schematically shown in Fig. 1. A high-pressure CO_2 pump (LabAlliance, Model SFC-24) were used for injecting liquid CO_2 into the reactor. The experiments were conducted according to the following procedure: starting precursors were dissolved in ethanol. A homogenous clear solution was obtained by stirring for 1 h with magnetic stirrer at room temperature. The vessel was then loaded with the clear solution, sealed and heated at 8 °C/min up to 150 °C. Simultaneously, CO_2 was injected into vessel at 15 MPa. After reaching the desired temperature and pressure, the experimental condition within the vessel was kept stable while the vessel was stirred at 100 rpm for 30 min. At the end of this time, the reactor was depressurized down to atmospheric pressure through a needle valve. The zirconia–silica powder was collected from the bottom of the vessel, subsequently washed for twice with 40 ml

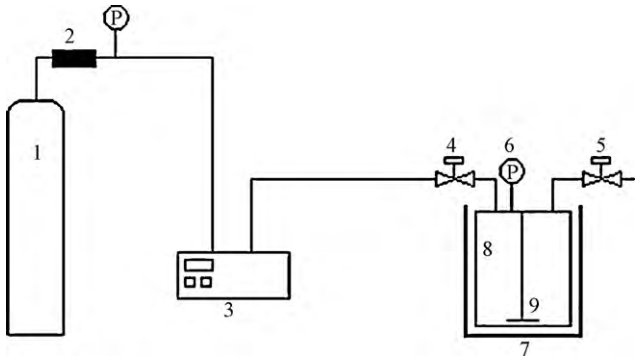

Fig. 1. Schematic representation of the set-up (1, liquid CO_2 tube; 2, filter; 3, CO_2 pump; 4, gas inlet valve; 5, depressure valve; 6, pressure gauge; 7, external heater; 8, vessel; 9, magnetic stirrer).

distilled water and ethanol. The washed solution was then centrifuged at 9000 rpm for 5 min, dried at 90 °C overnight and finally gently crushed in agate mortar. Heat treatment of the dried and crushed powder was carried out at 1000 °C and 1500 °C for 2 h. The crystallite size and the phases of the heat treated powders were determined by X-ray diffractometer (Rigaku, Miniflex) using Cu K_α radiation.

The surface area of the powders was determined using by BET (Quantachrome Nova 2200 E) instrument. The average particle size was calculated by the following equation from the surface area data, which is called d_{BET}. Scherrer formula was used to determine crystallite size from XRD named as d_{XRD}:

$$d_{BET} = \frac{6}{S.\rho} \quad (1)$$

ρ = density (g/cm^3) and S = surface area (m^2/g).

The density of the powders was determined using a helium gas pycnometers (Quantachrome Ultrapyc 1200e). Transmission electron microscopy (Jeol, JEM-2010F) and field emission scanning electron microscopy (Zeiss Supra 50 VP) were used to determine the powder morphology and average particle size. The degree of agglomeration was calculated as follows:

$$N = \frac{d_{BET}^3}{d_{XRD}^3} \quad (2)$$

N = the degree of agglomeration, d_{BET} = the average particle size from surface area, d_{XRD} = the average crystallite size from XRD [19].

3. Results and discussions

The XRD patterns of as-synthesized and calcined powders are shown in Fig. 2. As-synthesized powder is amorphous; however the tetragonal zirconia (t-ZrO_2) is formed after heat treatment to 1000 °C. Cristobalite (c-SiO_2) is detected in the region of 1500 °C, while t-ZrO_2 is the prevailing phase with a small amount of monoclinic ZrO_2 (m-ZrO_2). The crystallite size of c-SiO_2 is around 30 nm, as the size of t-ZrO_2 is varied from 8 nm to 30 nm at 1000 °C and 1500 °C, respectively. It is well know that m-ZrO_2 is the stable phase at low temperatures,

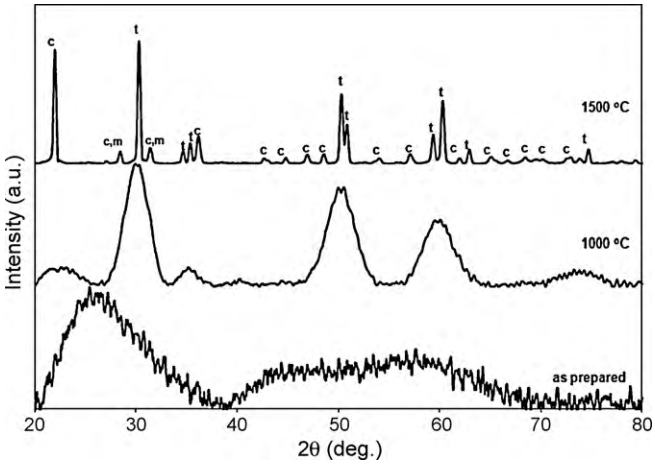

Fig. 2. XRD patterns of ZrO_2–SiO_2 nanocrystalline composite synthesized with supercritical CO_2 method and subsequently heat treated (t, tetragonal zirconia; m, monoclinic zirconia; c, cristobalite silica).

however, the tetragonal phase is the first formed on heat treatment. This is frequently attributed to several factors such as chemical effects, structural similarities between the tetragonal phase and the precursors amorphous phase as well as particle size effects [20]. Furthermore, the presence of lattice strains and defect centers on crystalline structure do not allow the tetragonal to monoclinic transformation to occur below a certain particle size (<∼30 nm) [21]. The stability of t-ZrO_2 can also be achieved by dopants such as CaO, MgO, Y_2O_3 and CeO_2. In this study, zirconia particles are embedded into the amorphous silica matrix at low temperature and cristobalite matrix at high temperature, which hinders the transformation of tetragonal to monoclinic phase.

Table 1
The surface area, density, crystallite size and agglomeration degree for ZrO_2–SiO_2 powders at 1000 °C.

Density (g/cm^3)	Surface area (m^2/g)	Crystallite size of ZrO_2 from XRD (nm)	Particle size from BET (nm)	Agglomeration degree, N (d^3_{BET}/d^3_{XRD})
2.6	171	8	13	4

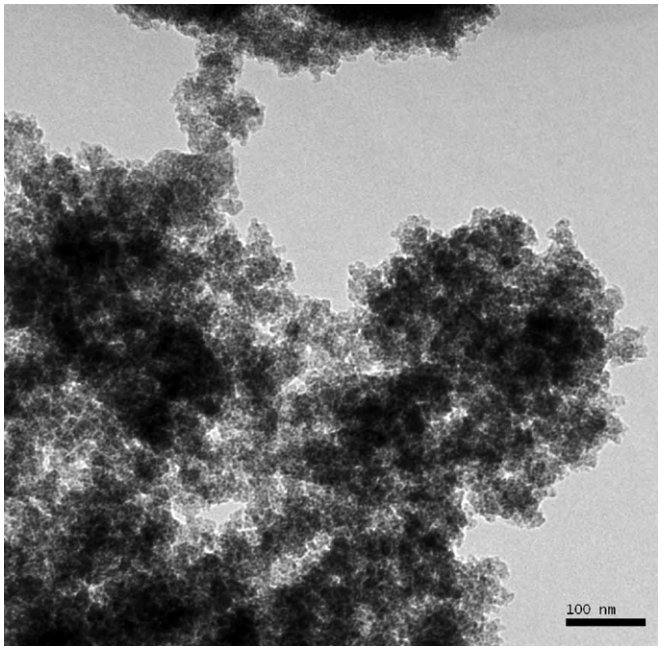

Fig. 4. TEM images of the ZrO_2–SiO_2 nanocrystalline composite powders calcined at 1000 °C for 2 h.

The results of surface area, density, particle size and crystallite size for ZrO_2–SiO_2 (50–50 vol.%) are shown in Table 1. The surface area of the samples calcined at 1000 °C is 171 m^2/g. The particle size calculated from surface area measurements for this sample, is 13 nm, however the crystallite size of the t-ZrO_2 is 8 nm.

The difference between particle and crystallite size measurements is due to the BET measurements where the surface of a volume is filled with a solid whereas XRD line broadening determines the coherently diffracting domain size. The ratio of the average particle size calculated from surface area (d_{BET}) and crystallite size determined from the Scherrer formula (d_{XRD}) is used to estimate the number of crystalline per particle, N, as a simple measure for the degree of agglomeration [17]. As this value become smaller or N value is close to unity, particles tend to approach their primary size, which may be classified as loose powders or soft-agglomerated powders.

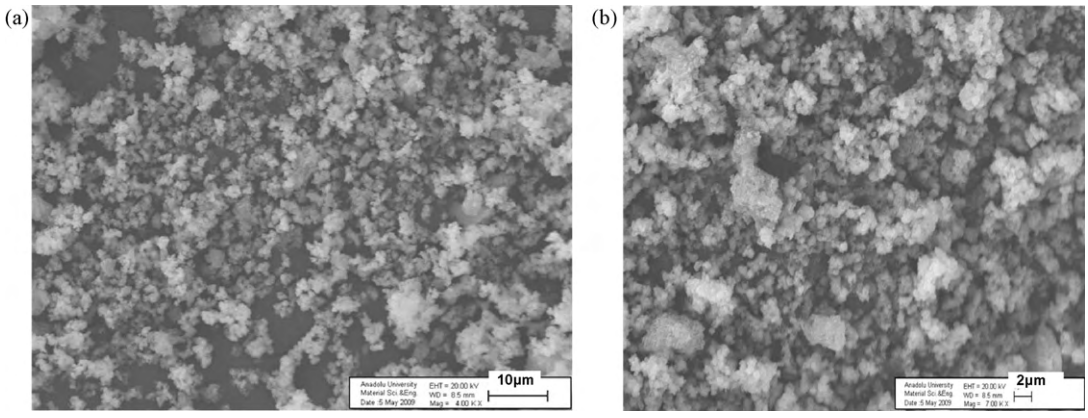

Fig. 3. SEM images of the ZrO_2–SiO_2 nanocrystalline composite powders calcined at 1000 °C for 2 h (a) 4000× and (b) 7000×.

SEM micrographs of the samples shown in Fig. 3 illustrate that particles are individual and have less contact with each other. The TEM image of sample in Fig. 4 shows equiaxed-rounded shape and a crystallite size was in good agreement with the XRD results.

4. Summary and conclusions

i. Supercritical fluid (CO_2) process has been demonstrated as a feasible method for the synthesis of soft-agglomerated zirconia–silica nanocrystalline powders.
ii. The XRD results showed that powders calcined at 1000 °C revealed only tetragonal zirconia phase, and then a mixture of tetragonal (major) with monoclinic (minor) zirconia and cristobalite (major) were formed after calcination at 1500 °C.
iii. The degree of powder agglomeration signifies that the synthesized particles consist of mostly primary particles with less agglomeration compared with powders synthesis by traditional techniques.
iv. SEM data showed that synthesized powders appeared to be mostly primary particles, which was in good agreement with agglomeration value.
v. Finally, the supercritical CO_2 method has been used successfully to control the agglomeration degree during the nanocrystalline powder synthesis.

Acknowledgement

The financial supports provided by the Scientific and Technological Research Council of Turkey (TUBITAK, project no: 107M367) are gratefully acknowledged.

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