Production of nano-sized yttria-stabilised zirconia powder by means of sol-gel supercritical fluid drying

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Zirconia-based ceramic materials have received much attention because of their technological significance. Yttria-stabilised zirconia (YSZ) exhibits high strength, high fracture toughness, and high thermal-stability and has many increasing and demanding engineering applications [1–3]. It is universally acknowledged that an unagglomerated globular powder with a narrow size distribution is the most desirable base material for compacting and sintering of ceramics with a desirable microstructure [4–6]. Several methods have been developed to produce nano-sized zirconia particles, such as hydrolysis of alkoxides [7, 8], hydrothermal treatment [9–11], and thermal hydrolysis of zirconium salts [12]. Since the nano-sized particles tend, to a certain degree, to agglomerate during traditional drying at room or elevated temperatures after synthesis, the particle size distribution in the produced powder is usually not very uniform even if using the hydrothermal treatment [11]. This is because in traditional drying, the surface tension at the liquid-gas interface within gel networks may cause large forces to act on the networks so as to break them down and make the system shrink, leading to agglomeration of the individual particles. For this reason, in the present work the supercritical fluid drying (SCFD) technique has been employed to prepare nano-sized zirconia powders.

In the SCFD, the gel is dried in the drying medium, such as ethanol, under its supercritical conditions (temperature and pressure). As is well known [13], at a constant volume, the critical point in the temperature-pressure diagram of a liquid represents the upper limit of the existence of the liquid. When the temperature and pressure of the system exceed the values corresponding to the critical point, i.e. under a supercritical condition, there will be no distinction between the liquid and the gas (vapor) and a single, undifferentiated fluid state of uniform density will exist. Under this condition, the surface tension present at the liquid-gas interface below the critical point disappears. Therefore, if the gel is dried using the SCFD technique, the gel networks will remain unchanged after drying so that the agglomeration of synthesized particles may be suppressed.

The starting materials used were zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 99% purity) and yttrium nitrate ($Y(NO_3)_3$, 99% purity). These materials were dissolved in ethanol in terms of 97 mol%ZrO_2 and 3 mol%Y_2O_3 as the starting solution with a concentration of $1M$. After adding acetic acid (CH_3COOH) as the complexing agent, the solution was heated in a thermostatic bath to 75 °C then the NH_4OH solution was gradually added with rigorous stirring until about pH 10[10]. After turning into a white sol, the solution was aged for 24 hr at room temperature to enable the sol to change into the gel. Then, the gel was repeatedly washed with distilled water by means of centrifuging until no precipitation occurred on examining with a $0.1M$ $AgNO_3$ solution. The washed gel was then dewatered with ethanol under rigorous stirring, collected by centrifuging, and dried by SCFD.

The SCFD with ethanol as the drying medium was conducted in an autoclave made of stainless steel. The critical conditions for the drying medium are 243 °C and 6.3 MPa [14]. So the supercritical conditions used here were 250 °C and 7.5 MPa. Prior to heating, the system was de-aired by an N_2 flow. Following the closure of the input and output of the system, the autoclave was first pre-heated to 150 °C at a rate of 100 K/h and then simultaneously heated and pressurised to 250 °C and 7.5 MPa, respectively. The duration of the supercritical condition was about 30 min. After that time, the ethanol was slowly vented and then the system was slowly cooled to room temperature with an N_2 flow. In order to investigate the thermal stability of the synthesized powder, some of the powder was calcinated at 1300 °C for 3 hr. Characterization of the powder was performed by X-ray diffraction (XRD, Rigaku D/max-3C X-ray diffractometer, CuK_α radiation) and transmission electron microscopy (TEM, Jeol 2000 FXII).

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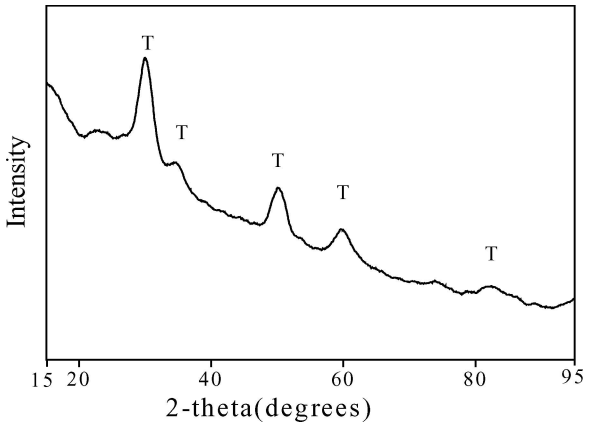

Figure 1 XRD pattern of the as-produced powder.

The XRD pattern of the produced powder is represented in Fig. 1. Clearly, the diffraction peaks are quite wide, indicating that the particles are very small. Analysis of the pattern shows that the diffraction peaks stem from the tetragonal zirconia phase without any information from the yttria, demonstrating that the yttria has fully dissolved into the zirconia. This stabilizes the tetragonal phase of zirconia, which is consistent with the zirconia-yttria phase diagram [15]. Fig. 2 shows the XRD pattern for the sample calcinated at 1300 °C. After calcinating, the diffraction peak position and shape remain unchanged. This indicates that the tetragonal phase of the powder remains unchanged, showing a strong thermal stability of the produced powder.

To evaluate the grain size of the powder, the Scherrer equation was used [10]. This equation is written as

$$D = \frac{0.89\lambda}{\Delta\beta \cos\theta} \quad (1)$$

where λ is the wavelength of X-ray (1.5418 Å for CuK_α radiation), θ is the Bragg angle, and $\Delta\beta$ is the full width at half the maximum intensity of the peak. According to Equation 1, the grain size is about 6 nm for the as-produced powder and 7 nm for the calcinated one.

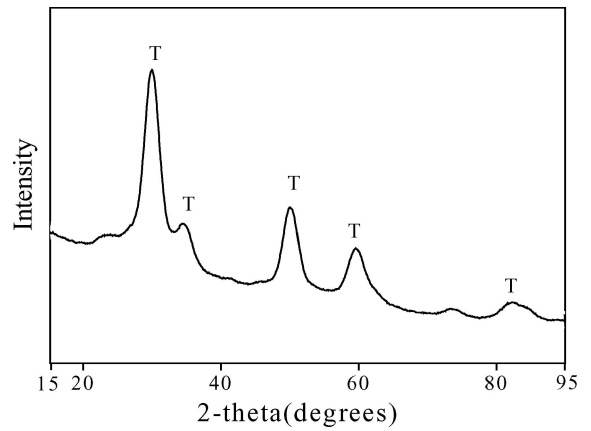

Figure 2 XRD pattern of the powder after calcination at 1300 °C.

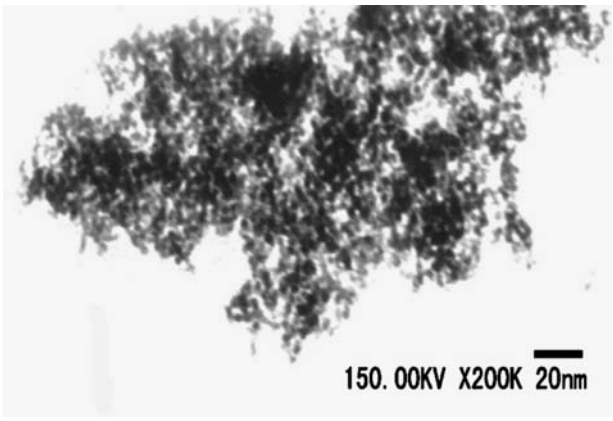

Figure 3 Transmission electron micrograph of the as-produced powder.

A typical transmission electron micrograph for the as-produced powder is shown in Fig. 3. The particles have a very small size (<10 nm) and have some agglomerated but the extent is relatively small. Therefore, the particle size exhibited in Fig. 3 is consistent with that estimated from the Scherrer equation.

In summary, a sol-gel supercritical fluid drying route has been used to synthesize nano-sized 3 mol% Y_2O_3-ZrO_2 powder. The produced powder has a particle size of less than 10 nm and possesses a single tetragonal phase. The particles in the powder have some agglomeration but the extent is relatively small. Moreover, there is a strong thermal stability for the powder produced by this technique.

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