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Preparation of Ultrafine Zirconia Powder by Emulsion Method

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Abstract

Ultrafine 14 nm 3 mol% Y_2O_3 stabilized tetragonal ZrO_2 powder was prepared by emulsion processing. The obtained particles were weakly agglomerated into polyhedral or spherical shaped powders. The powder characteristics were investigated by using X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma spectroscopy (ICP), nitrogen adsorption (BET model) and thermal analysis (DTA–TG). The experiments indicated that the heterogenous distillation used in the process was an effective method to remove residual water in the gel-precipitate and reduce the formation of strong agglomerates. The powder presented good formability and sinterability.

1 Introduction

Ceramic materials which consist of 100% yttria-doped tetragonal zirconia polycrystals (Y-TZP) exhibit a high strength and toughness compared to other ceramics. The ceramic powder characteristics of particle size, shape, size distribution and agglomeration state have very important influences on the sintering behaviour and final microstructure. In order to obtain dense and pure tetragonal zirconia ceramics with small grain sizes, special requirements must be fulfilled by the powders used for the sintering process. These ceramic powders must be homogeneous in composition and highly sinter-active (low sintering temperature) in order to decrease grain growth during sintering. Previous studies have shown that ultrafine, unagglomerated, soft powders can lower sintering temperature and produce fine grain microstructure.[1]

With a drastic decrease in the grain size and, subsequently, increasing of interfacial surface areas, some improved or new properties of ceramic materials could be expected. For instance, if the grain sizes of ceramics are decreased down to the nanometre scale, the higher fraction of atoms located in the grain boundary regions will result in the rapid diffusivities, enhanced solubilities and low temperature ductility.[2]

Recently, considerable effort has been given to the chemical synthesis of ultrafine ceramic powders via both aqueous and vapour phase routes.[3] A noteworthy problem is that the ultrafine powders could easily contain hard agglomerates, which would postpone the densification process. To solve this problem, Kanai[4] and Ramamurthi[5] have reported on emulsion methods for the preparation of ultrafine and unagglomerated powders.

In this paper, the synthesis of ultrafine ZrO_2–3 mol% Y_2O_3 powder using the emulsion method has been described. In this method, water droplets containing zirconium ions are suspended and stabilized in an organic non-polar solvent by addition of an appropriate surfactant. The emulsion droplets are gelled by ammonia gas, and the gel droplets are then stabilized by removing water during heterogeneous distillation. The powder characteristics and its sintering properties have also been investigated.

2 Experimental Procedure

Zirconyl nitrate, $ZrO(NO_3)_2{\cdot}nH_20$ and yttrium nitrate $Y(NO_3)_3{\cdot}6H_2O$ (both with purities >99%) were selected for the preparation of Y-TZP powders and dissolved in distilled water. $ZrO(NO_3)_2{\cdot}nH_2O$ was chosen over $ZrOCl_2{\cdot}nH_2O$, since nitrogen-containing compounds lead to cleaner and easier burn-out compared with chloride-containing compounds. The concentrations of Zr^{4+} and Y^{3+} in the above two solutions were exactly determined by chemical analysis in order to precisely control the chemical compositions of the prepared powders.

The mixed solution was poured into a 5000 ml

beaker which was charged with xylene. The volume ratio of solution to xylene was 1:10. A surfactant, Tween 80 with 0·2 vol% of xylene, was slowly added to the beaker while stirring. Small solution droplets were thus developed and an emulsion was formed in which the droplets were stabilized by the surfactant present. The emulsion was magnetically stirred for 45 min. Ammonia gas was bubbled through the suspension using a glass tube for 10 min to gel the emulsion droplets. The suspension was then transferred to a flask for distillation using the apparatus shown in Fig. 1. The temperature of the suspension was increased by heating and maintained at 144°C which is the boiling point of xylene. At this time, the distillate was xylene only. The distillation treatment was finished after the temperature had stabilized at 144°C for about 45 min. The powder was isolated by filtering, dried at 160°C for 12 h and calcined at 600°C for 1 h and 700°C for 1 h. The whole process is summarized in Fig. 2.

Powder calcined at 700°C was cold isostatically pressed at 200 MPa into pellets (7·2 mm in diameter, 1–2 mm in thickness) with the use of PVA. Sintering was conducted at 1250°C for 30 min. The grain size was determined by scanning electron microscope (SEM) observation and the sintered densities were measured by the Archimedes method in distilled water.

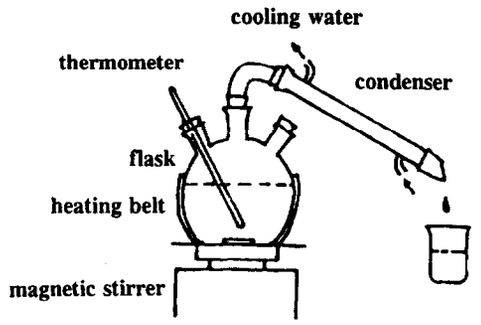


Fig. 1. Apparatus used for heterogeneous distillation.

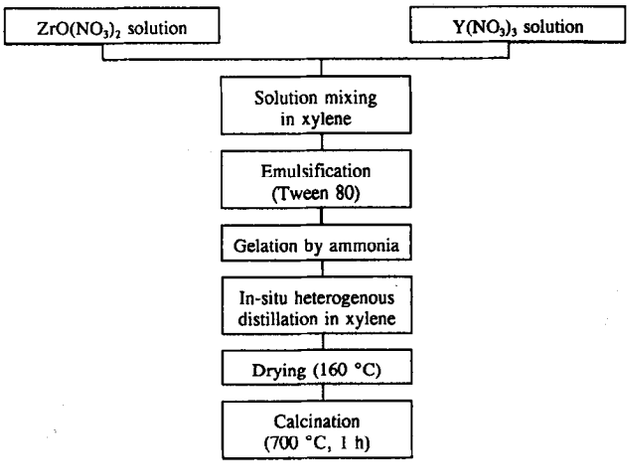


Fig. 2. Processing diagram of powder preparation by emulsion method.

3 Results and Discussion

3.1 Powder characteristics

The chemical compositions of the powder, as determined by X-ray fluorescence spectroscopy (XRF) and inductively coupled plasma spectroscopy (ICP), are given in Table 1. The yttria composition of the prepared powder showed a small amount of deviation from the designed composition by the XRF method. The X-ray diffraction study on the powder identified the tetragonal phase after calcination.

The morphology of the particles was observed by transmission electron microscopy (TEM). It was found that the prepared powders were composed of nanometre-sized crystallites, which in turn were loosely attached together to form powders of polyhedral or spherical shape, as seen from Fig. 3. The specific surface area of the powder calcined at 700°C measured by the BET

Table 1. Chemical analysis results of prepared powder

Y_2O_3 content by XRF (mol%)	*Impurities measured by ICP (wt%)*			
Y_2O_3	SiO_2	MgO	HfO_2	CaO
2·8	0·022	< 0·007	0·78	0·47

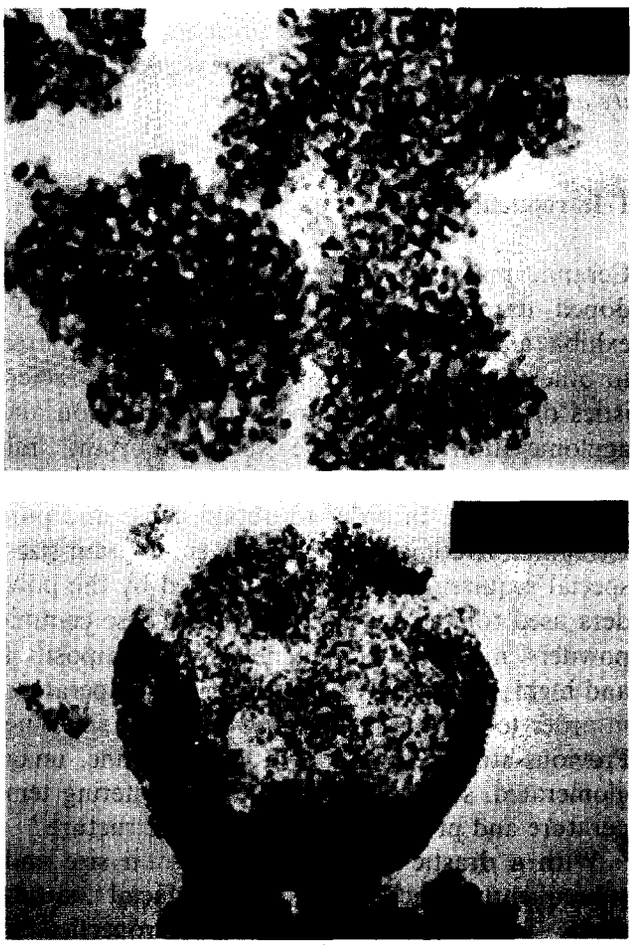


Fig. 3. TEM micrograph of the prepared powder.

method was 52·5 m^2 g^{-1} which was equivalent to an 18·7 nm crystallite.

This result was in good agreement with the average crystallite size of 14 nm obtained from the TEM micrograph in Fig. 5(D). From this fact, it could be concluded that the agglomeration strength among the crystallites in the powder was very weak and the formation of hard agglomerates was basically avoided.

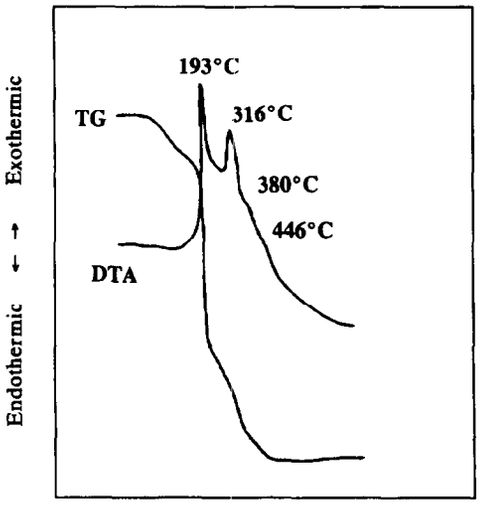
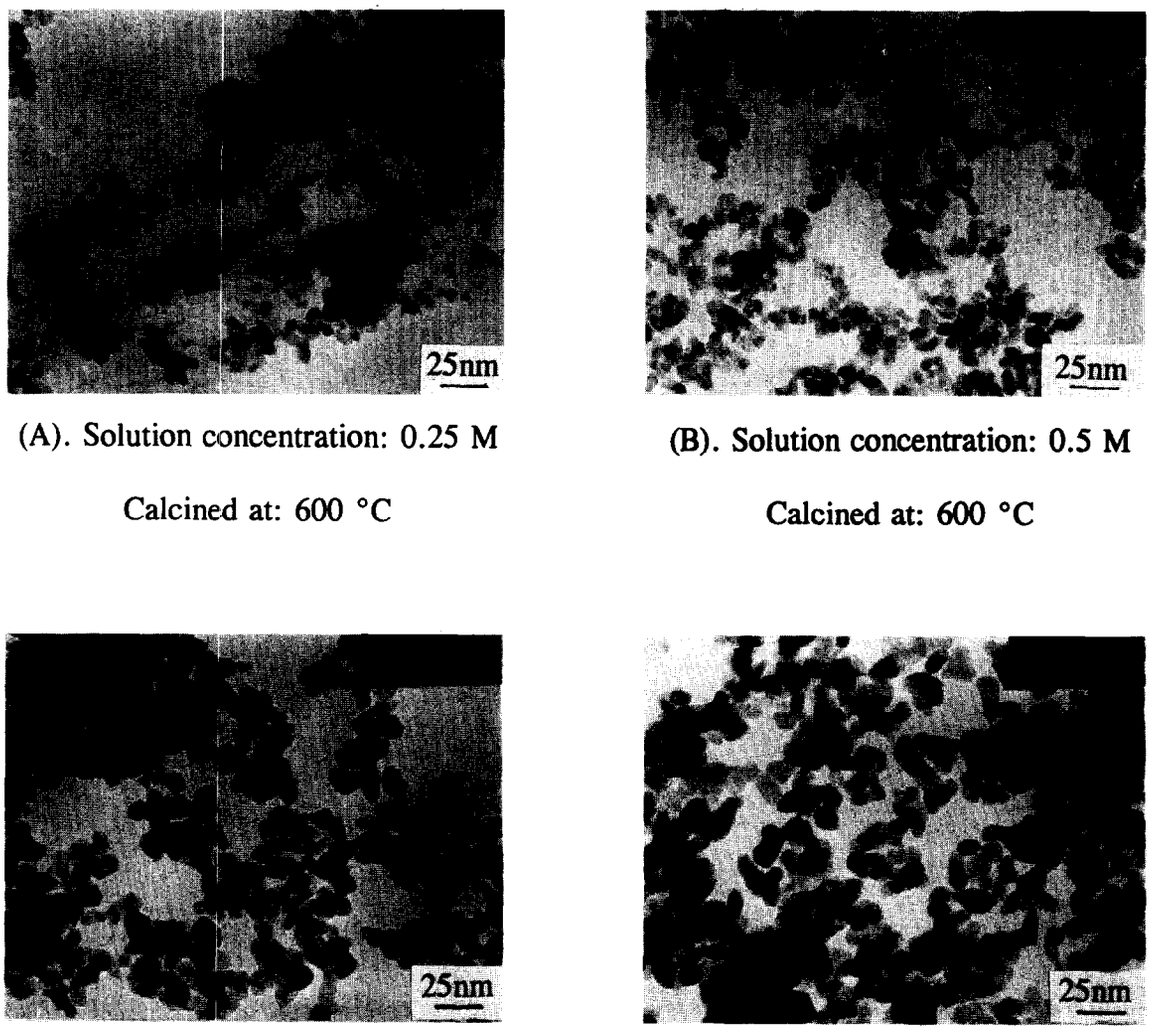


Fig. 4. DTA–TG traces of the prepared powder.

The thermal processing and crystallization behaviour of the powder were investigated by using DTA–TG methods as shown in Fig. 4. Two obvious exothermic peaks were found at 193 and 316°C and they could be attributed to the organic substance burn-out and nitrate decomposition. Another two small exothermic peaks around 380 and 446°C could be related to the debonding of oxyhydrogen groups and the beginning of crystallization, respectively.

3.2 Effects of solution concentration and calcination temperature on crystallite size

Figure 5 shows TEM micrographs of the powder



(A). Solution concentration: 0.25 M

Calcined at: 600 °C

(B). Solution concentration: 0.5 M

Calcined at: 600 °C

(C). Solution concentration: 0.25M

Calcined at:700 °C

(D). Solution concentration: 0.5 M

Calcined at: 700 °C

Fig. 5. The effects of solution concentration and calcination temperature on crystallite size.

prepared with different solution concentrations and at different calcination temperatures. The average crystalline size in Figs 5(A) and (B) was about 8–10 nm, while that in Figs 5(C) and (D) ranged from 12 to 14 nm. From this observation, it could be suggested that the crystallite size is mainly dependent upon the calcination temperature rather than the solution concentration.

3.3 Sintering behaviour

High green densities of over 50% TD were obtained after pressing. Sintering was performed using the following schedule: ambient to 800°C at 10°C min^{-1}; 800 to 1100°C at 6°C min^{-1}; 1100 to 1250°C at 3°C min^{-1}; holding at 1250°C for 30 min and then cooled naturally. Sintered zirconia in 100% tetragonal phase with a density of 97% TD and an average grain size of 0·22 μm was obtained.

4 Conclusions

Ultrafine Y_2O_3 stabilized tetragonal ZrO_2 powder was successfully prepared by the emulsion method. The prepared powders take advantage of forming weak agglomerates in the preparation process which facilitate the compaction of nanometre-scale primary particles. Experimental results showed that the calcination temperature had a significant influence on the crystallite size. Preliminary sintering studies indicated good sinterability of the powder.

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