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Preparation of Nanometre-Sized ZrO_2/Al_2O_3 Powders by Heterogeneous Azeotropic Distillation

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Abstract

Nanometre-sized ZrO_2/10 vol% Al_2O_3 composite powder without hard agglomerates was prepared by the process of heterogeneous azeotropic distillation. Interfacial chemical bonding between $Zr(OH)_4$–$Al(OH)_3$ and n-butanol was determined by Fourier transform infra-red spectroscopy. The average particle size of the composite powder was about 20 nm in diameter, and the powder can be sintered up to theoretical density (>99%) at 1300°C for 4 h. The mechanisms by which azeotropic distillation in n-butanol prevented agglomeration were attributed to both the decrease of capillary force between the hydrates and the chemical adsorption of $C_4H_9O^-$ base on the surface of the hydrates. © 1997 Elsevier Science Limited. All rights reserved.

Introduction

There is currently a growing interest in nanometre-sized powders because of their novel properties such as catalytic activity, sintering forging, low-temperature sintering, etc.[1] However, the superfine powders easily form aggregates because of their very high surface energy, which has a deleterious effect on their sintering activity, etc. It is, therefore, very important to prevent the powders from agglomerating.

Chemical co-precipitation is a low-cost method to fabricate oxide powders compared with other processes (such as sol–gel, chemical or physical vapour deposition). However, the process suffers from the disadvantage of producing hard agglomerates during drying and calcining procedures due to the high surface tension stress and hydrogen bonding of the hydrate particles.[2] The key issue to decrease agglomeration has been considered to decrease the tension stress and to overcome hydrogen bonding by replacing water with an organic solvent, since water has a very high surface tension stress and strong hydrogen bond.[3] Ethanol washing of hydrates is a common way to substitute for H_2O, but this substitution is limited and some amount of H_2O molecules remain in the gels owing to the fact that washing is only carried out several times. Another disadvantage of this method is the expense of a large amount of alcohol. Surface treatment of hydrates by organic polymer surfactants has also been used to lower the degree of agglomeration.[4] Although this is an economical route and the deagglomeration effect is comparable with the alcohol washing process, agglomeration cannot be completely eliminated because only part of the water is replaced by the organics that usually have lower surface tension stress and less ability to form hydrogen bonds.

Recently, Qu *et al.*[5] reported a new processing method, heterogeneous azeotropic distillation (HAD), based on chemical co-precipitation, to prepare nanometre-sized tetragonal zirconia powder that was free of hard agglomeration and could be sintered at very low temperature (1250°C). Unfortunately, the mechanism and preparation of composite powders by this new process have not been reported.

In this research, we synthesize ZrO_2/10 vol% Al_2O_3 composite powders with nanometre size and without agglomerates, using the HAD technique, and study the process mechanism in detail.

Experimental Procedures

The starting materials are $ZrOCl_2.8H_2O$ (AR, Shanghai No. 51 Chemical Factory), Y_2O_3 (AR, Shanghai Yuelong Chemical Factory) and $Al(NO_3)_3.6H_2O$ (AR, Shanghai Zhengshing Chemical Factory). Y_2O_3 was first dissolved in hydrochloric acid, followed by $ZrOCl_22.8H_2O$, to give a mixture containing 2·8 mol% Y_2O_3. The solution of the two compounds was mixed with $Al(NO_3)_3.6H_2O$,

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the ratio being 10% Al_2O_3. The solution containing Al^{3+}, Y^{3+} and Zr^{4+} was chemically co-deposited in water by adjusting the pH value to 8–9 using $NH_3.H_2O$ and NH_4HCO_3. The $Zr(OH)_4$–$Y(OH)_3$–$Al(OH)_4$ gel was washed with water until no white deposit of AgCl was observed in the waste water, as tested by $AgNO_3$. The washed cake was blended with n-butanol using mechanical stirring and distilled in the apparatus shown in Fig. 1. The azeotrope of 44·5 wt% water and 55·5 wt% n-butanol was first co-evaporated at 93°C, the azeotropic boiling point; the components were separated, after cooling, by passing through two condensers and a water trap. During this process, n-butanol came back to the flask and continued to be used until the temperature rose to 117°C, the boiling point of n-butanol, indicating that all the water had been removed from the hydrate gels according to the principle of azeotropic distillation. After the distillation was complete, the gels were dried at 120°C for 2 h, calcined at 750°C for 2 h, and finally transformed into tetragonal zirconia (t-ZrO_2) and γ-alumina (γ-Al_2O_3). The calcined composite powder was pressed at 500 MPa to form a platelet of dimensions ϕ 12 mm × 3 mm, and sintered at 1000–1500°C for 4 h. In order to compare the effect of distillation on deagglomeration, a non-distilled powder with the same composition as the distilled powder was also prepared and characterized by the same processes.

Particle size and morphology were observed by transmission electron microscopy (TEM; JEM 200cx, Japan). Specific surface area and surface chemical bonding were measured by the BET method (Shanghai Analysis Factory) using N_2 adsorption and Fourier transform infra-red spectroscopy (FTIR; Nicolet 520 FT-IR, USA), respectively. Pore distribution in the green bodies was analysed by mercury spectroscopy (Shanghai Analysis Factory). Evaporated gases during calcination of the gels were tested by mass spectrometry (MS; Hitachi M-80, Japan). Density of sintered specimens was measured using Archimedes' method. The surface microstructure of the composite was observed by scanning electron microscopy (SEM; Cambridge S-250, UK).

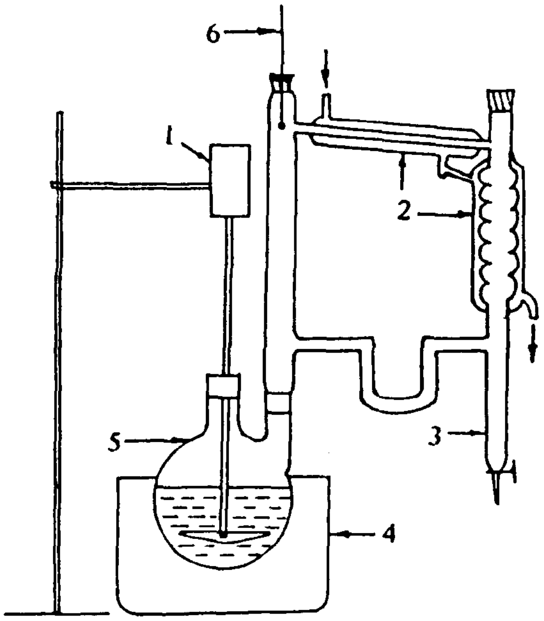

Fig. 1. Schematic diagram of the heterogeneous azeotropic distillation apparatus: (1) electric stirrer; (2) condenser; (3) water trap; (4) thermal block; (5) flask; (6) thermometer.

Results and Discussion

Agglomeration control by distillation

Figure 2 shows TEM photographs of ZrO_2/10 vol% Al_2O_3 powders that were distilled [Fig. 2(A)] and not distilled [Fig. 2(B)]. It can be seen that the composite particles were dispersive for distillation but agglomerated when distillation was not performed; specific surface areas based on BET measurement were 45 m^2 g^{-1} and 30 m^2 g^{-1}, respectively. Owing to the crystallites of the powders being very small, it is difficult to distinguish between zirconia and alumina. Figure 2 also shows

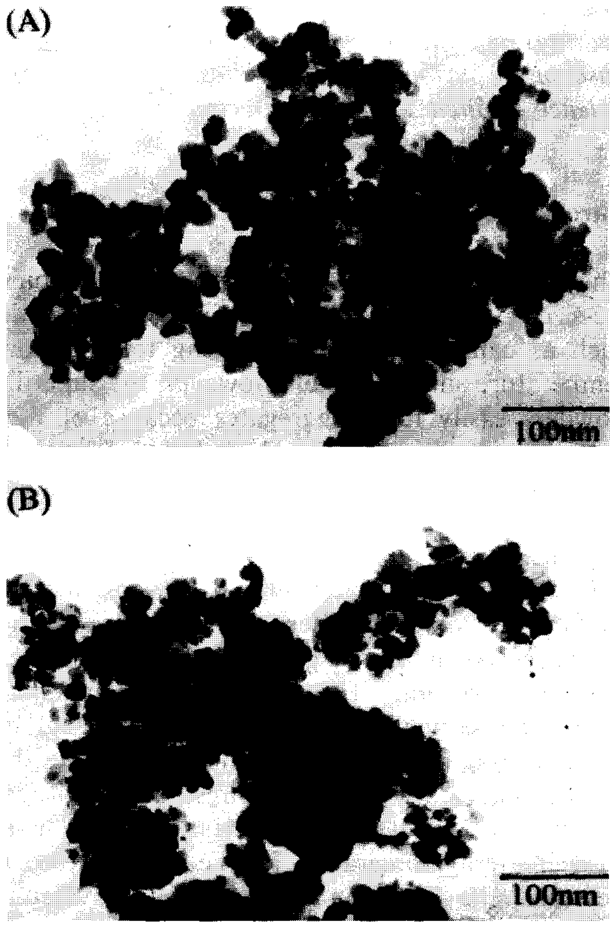

Fig. 2. TEM photographs of ZrO_2/10 vol% Al_2O_3 composite powder: (A) produced with azeotropic distillation, (B) no azeotropic distillation.

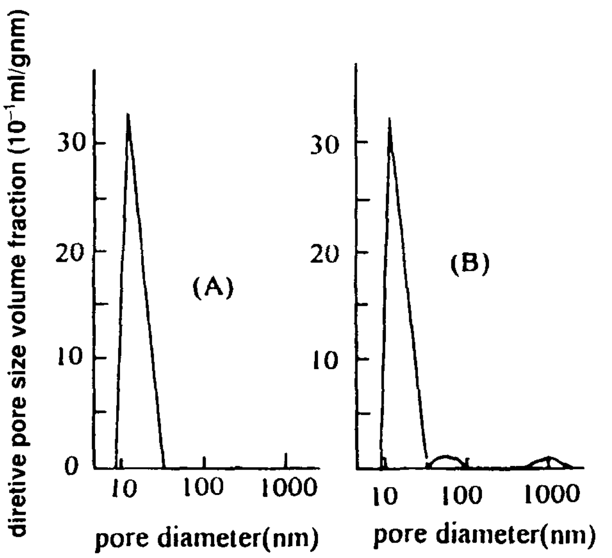

Fig. 3. Pore size distribution of dry-pressed articles of ZrO_2/10 vol% Al_2O_3 powder: (A) produced with azeotropic distillation, (B) no azeotropic distillation.

that the two kinds of powder each contained particles about 20 nm in diameter. However, the green bodies of the powders had different pore distributions, as shown in Fig. 3. For distilled powders, only one peak was located at 10–50 nm pore diameter, the same order as the particle size, indicating that the powder contained few agglomerates. However, for powders that were not distilled, three pore size distributions were found in the green bodies: one at 10–50 nm corresponding to the pores between the crystalline particles and others at 50-90 nm and 800–1300 nm corresponding to the vacancies between agglomerates. Therefore, heterogeneous azeotropic distillation is an effective way to eliminate agglomeration produced in the chemical co-precipitation process.

Mechanism of preventing agglomeration

The agglomeration-free powder is first attributed to a decrease of the surface tension stress between hydrate particles. The non-distilled gels have a large surface tension stress of water, 72·75 dyn cm^{-1} at 20°C, causing agglomeration of the hydrate particles. On the contrary, the water in the distilled gels has been replaced by n-butanol which has a low surface tension stress, 25 dyn cm^{-1} at 20°C, leading to a decrease of the degree of agglomeration. This effect is just like alcohol washing and surfactant treatments of the hydrates, reported in the literature.[3,4]

The above explanation was supported by Fig. 4, a mass spectrum of CO_2^+ ($m/e = 44$), H_2O^+ ($m/e = 18$), $C_4H_{10}O^+$ ($m/e = 74$), $C_8H_{18}O^+$ ($m/e = 130$). It was found that CO_2^+ peaks at 130°C, 193°C and 500°C, $C_4H_8{}^+$ peaks at 400°C, and no H_2O^+ peak at any temperature appeared for the distilled gels [Fig. 4(A)], indicating that H_2O was completely replaced by n-butanol which decomposed into CO_2 and C_4H_8. By comparison, the nondistilled gels only had a H_2O^+ peak at 100–150°C [Fig. 4(B)], i.e. some amount of H_2O still remained between the gel particles even after the drying process at 120°C for 2 h. These experimental results agree with those of Qu *et al.*[5]

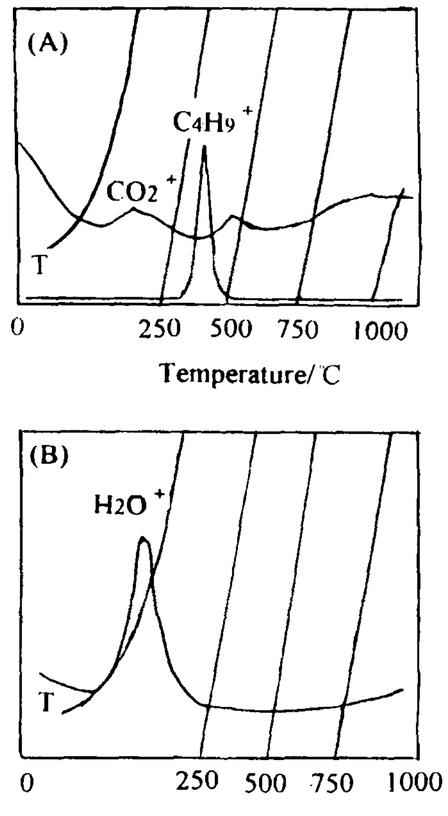

Fig. 4. Mass spectra of (A) distilled ZrO_2/10 vol% Al_2O_3 powder, (B) nondistilled powder.

Secondly, Van der Waals' bonding instead of hydrogen bonding may be responsible for eliminating agglomeration by distillation treatment. In fact, the following surface reaction between $Al(OH)_3$, $Y(OH)_3$, $Zr(OH)_4$ and n-butanol may take place during distillation:

$$M(OH)_n + HOC_4H_9 \rightarrow H_2O + (OH)_{n-1}\text{-}M\text{-}O\text{-}C_4H_9 \quad (1)$$

where M stands for Al, Y and Zr elements, i.e. the surface OH groups of the hydrates were substituted by OC_4H_9 which corresponds to hydrophilicity and hydrophobicity, respectively. As a result, strong hydrogen bonding between the hydrate gels with H–O–H bridges became a Van der Waals' bond with O–C_4H_9 bridges after the gels were distilled.

This replacement was verified by MS spectra in Fig. 4(A), which shows that n-butanol was chemically absorbed on the gel surface because it still remained despite drying at a temperature higher than the boiling point of n-butanol, 117°C. Furthermore, transformation from a nonhomogeneous mixture of gel and n-butanol before distillation into a homogeneous system after the HAD process was observed. This phenomenon may demonstrate that chemical bonds were formed between the gel surface and n-butanol.

As direct experimental data of the chemical bond, FTIR spectra are shown in Fig. 5. We found that all the curves in Fig. 5 had the same adsorption peaks at 3428, 1622, 875 and 509 cm^{-1}, which are respectively attributed to vibrations of O–H, C=O, Al–O and Zr–O bonds, C=O coming from absorbed CO_2 in air on the surface of the gels. The peaks at wavenumbers 2922 and 2852 cm^{-1} correspond to vibration of C–H bonds, and at 1446 cm^{-1} to vibration of C–C bonds, from absorbed n-butanol on the gel particles. Now, we concentrate on the adsorption bands at 1020–1084 cm^{-1}, which are generated by vibration of Al–O and C–O bonds. It is found that the nondistilled gels have one Al–O bond adsorption at 1084 cm^{-1} because there is no n-butanol coating on the hydrates [Fig. 5(A)]. The mechanical mixture of n-butanol and gel has two separate vibration adsorptions of C–O bonds at 1084 cm^{-1} and 1045 cm^{-1} [Fig. 5(B)]. This implies that there is weak chemical bonding of $C_4H_9O\text{–}M(OH)_{n-1}$ at the interface between n-butanol and the gel. Also, for distilled hydrates with n-butanol, the degree of separation of the C–O and Al–O bond vibrations becomes more obvious, the two wavenumbers becoming three at 1084, 1045 and 1029 cm^{-1}. This decrease and separation of the wavenumbers of C–O bonds may result from Al, Zr, Y atoms partially replacing H atoms, since the larger the atomic weight, the smaller the wavenumbers of IR adsorption based on IR principles. Therefore, the surface reaction [eqn (1)] holds.

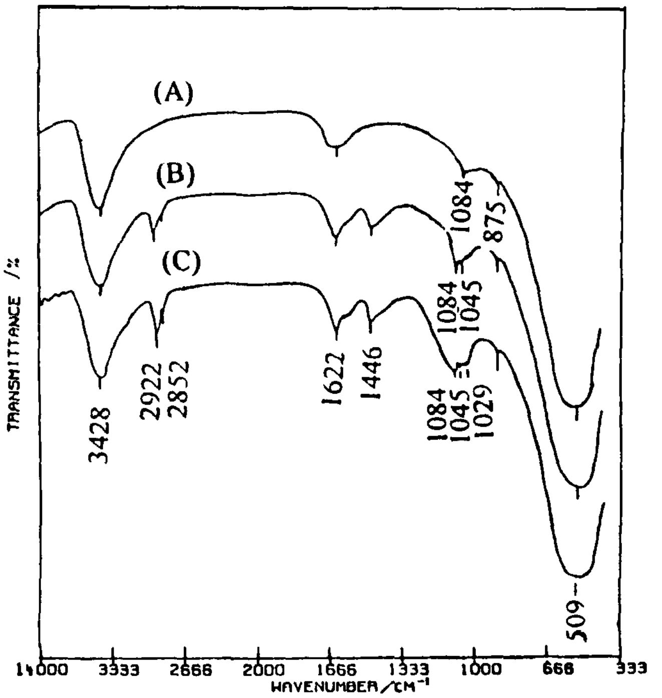

Fig. 5. FTIR spectra of $Zr(OH)_4$–$Y(OH)_3$–$Al(OH)_3$ gels dried at 120°C for 2 h: (A) no azeotropic distillation, (B) mechanical mixture of n-butanol and the gels, and (C) azeotropic distillation.

Sintering behaviour

Figure 6 shows the relative density as a function of sintering temperature for ZrO_2/10 vol% Al_2O_3 powders. Sintering of the distilled powder started at 1100°C and finished at 1300°C, giving a density of >99·0% theoretical [Fig. 6(A)]. However, the nondistilled powder had start and end sintering temperatures of 1400°C and 1600°C [Fig. 6(B)] respectively, being 300°C higher than those of the distilled powder. These results show that heterogeneous azeotropic distillation is a powerful process to decrease sintering temperature, which results from the distilled powders having no hard agglomerates. It should be noticed that the crystalline phase of the alumina is γ-Al_2O_3 at sintering temperature below 1100°C, whereas the γ-Al_2O_3 will be transformed into α-Al_2O_3 if sintering proceeds above 1100°C. This resulted in relative density errors since the theoretical density is calculated on the basis of the density of α-Al_2O_3. However, since there was only 10 vol% alumina in the composite, the density error was ignored.

The microstructures of the bodies sintered at 1500°C for 4 h are shown in Fig. 7. The distilled powder had a very uniform sintered microstructure with few pores [Fig. 7(A)], but many connective pores were found for the sintered body of the nondistilled powder [Fig. 7(B)]. At 1500°C, the sintered specimens of both powders had almost

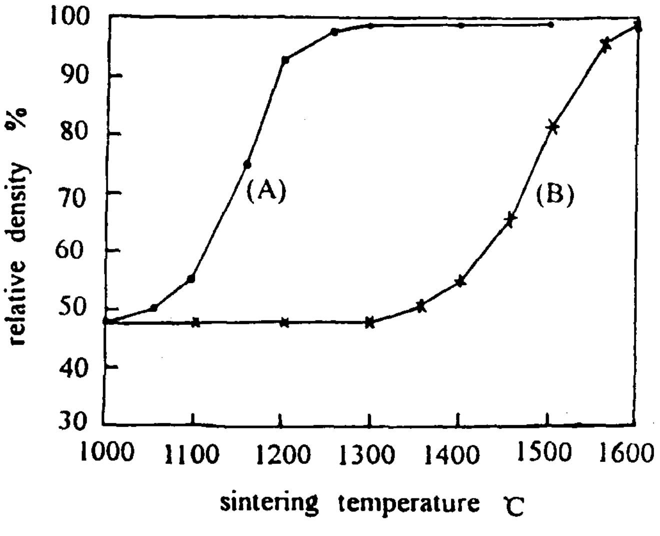

Fig. 6. Relative density as a function of sintering temperature for ZrO_2/10 vol% Al_2O_3 powders: (A) produced with azeotropic distillation, (B) no azeotropic distillation.

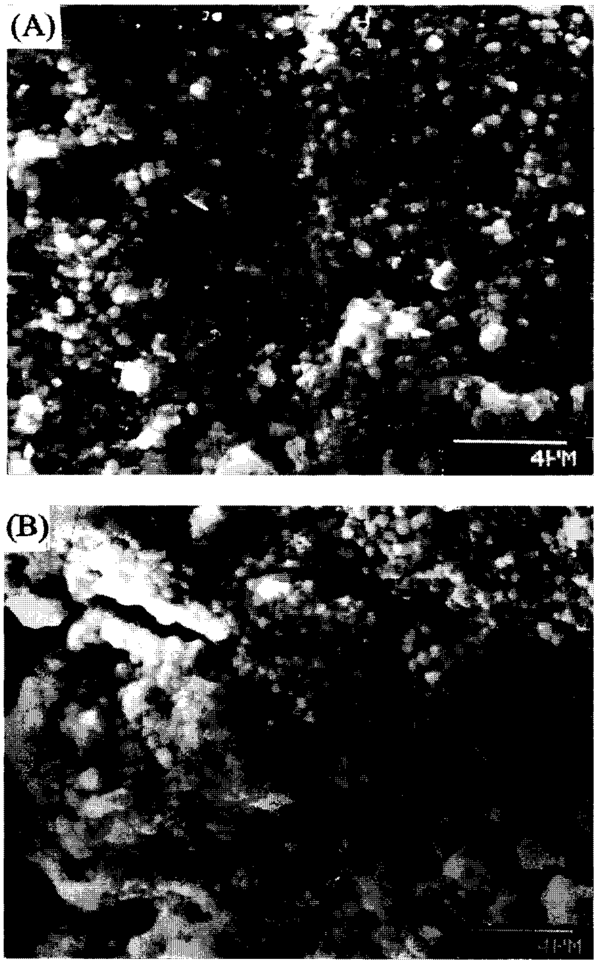

Fig. 7. SEM photographs of surface microstructures of ZrO_2/10 vol% Al_2O_3 powder sintered at 1500°C for 4 h: (A) no azeotropic distillation, (B) azeotropic distillation.

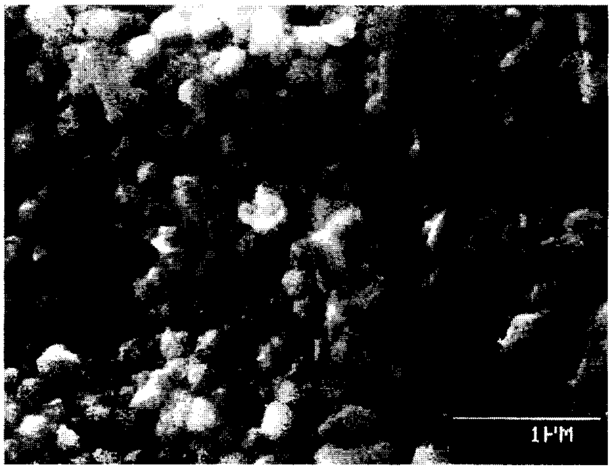

Fig. 8. SEM photograph of surface microstructure of ZrO_2/10 vol% Al_2O_3 powder sintered at 1300°C for 4 h, powder produced by azeotropic distillation.

same grain size of about 0·5 μm. Moveover, the distilled powders of both zirconia and alumina had average grain sizes of about 0·2 μm after sintering at 1300°C for 4 h (Fig. 8). All these microstructural observations can be explained on the basis of the new process preventing agglomeration. Although the sintered body of the nondistilled powder has the same grain size as the distilled one [Figs 7(A), (B)], many connective pores exist when distillation is not carried out [Fig. 7(B)]. Because the distilled powder is agglomerate-free, the densification of the powder proceeds much more easily than in the nondistilled powder containing agglomerates.

Conclusions

(1) Agglomeration-free nanometre-sized ZrO_2/10 vol% Al_2O_3 composite powder was prepared by heterogeneous azeotropic distillation. The average particle size is 20 nm with specific surface area of 40 m^2 g^{-1}.

(2) The mechanisms preventing agglomeration of the distilled powder are a decrease of surface tension stress and elimination of hydrogen bonding between $Zr(OH)_4$–$Y(OH)_3$–$Al(OH)_4$ gel particles, using n-butanol to replace water.

(3) The distilled composite powder can be sintered up to >99% theoretical density at 1300°C for 4 h. The sintered specimen had a very uniform microstructure with average grain size 0·2 μm.

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