

PREPARATION OF NANOMETER ZrO_2 -8 % Y_2O_3 POWDERS BY AZEOTROPIC DISTILLATION PROCESSING^①

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ABSTRACT Gels of $\text{Zr}(\text{OH})_4$ and $\text{Y}(\text{OH})_3$, prepared by the chemical coprecipitation method, were effectively dehydrated by the azeotropic distillation processing. Because of the removal of interparticle free water, replacement of surface hydroxyl groups with butoxy groups and steric effects of *n*-butanol, close approach of gel particles and Zr-O-Zr chemical bond formation between them were prevented. Nanometer ZrO_2 -8 % (mole fraction, %) Y_2O_3 powders prepared by this processing, with the average particle size of 16 nm, can be sintered to 98.5 % TD at 1450 °C for 2 h with an average grain size of ceramic of 0.3 μm .

Key words ZrO_2 -8 % Y_2O_3 nanometer powder chemical coprecipitation method azeotropic distillation hard agglomerate

1 INTRODUCTION

It is well known that sintering temperature will be greatly decreased due to preparation of ultrafine and homogeneous powders. As a result, dense ceramics without porosity are obtained with grain size of several micrometers^[1]. Compared to conventional solid-state reactions, wet chemical methods such as chemical coprecipitation can produce homogeneous and active powders. However, a usual problem with this method is the formation of hard agglomerates which leads to a higher sintering temperature and harmful changes of microstructure such as heterogeneous porosity and abnormal grain growth. So hard agglomerates must be avoided for good sinterability of ceramic powders. The key to avoid the formation of hard agglomerates is to remove absorbed water and nonbridging hydroxo groups of gels. For example, alcohol washing can remove free water and replace hydroxyl groups with ethoxy groups, so the occurrence of hard agglomerates is greatly reduced^[2]. In addition, surface active agent^[3], freeze-drying^[4] and azeotropic distillation^[5] can also control agglomeration to different extent.

As one of functional ceramics, ZrO_2 -8 % (mole fraction, %) Y_2O_3 has found wide applications in oxygen sensors, solid oxide fuel cell (SOFC) and electrochemical oxygen pumps. In this paper, $\text{Zr}(\text{OH})_4$ gels will be dehydrated by *n*-butanol azeotropic distillation processing (compared to carbon tetrachloride^[6] and xylene^[7], *n*-butanol has the advantages of lower boiling point and no harm to human) in order that the formation of hard agglomerates can be effectively prevented and nanometer ZrO_2 -8 % Y_2O_3 powders with good sinterability can be prepared.

2 EXPERIMENTAL PROCEDURE

According to a nominal composition of ZrO_2 -8 % Y_2O_3 , the mixed solutions of ZrOCl_2 and $\text{Y}(\text{NO}_3)_3$ were slowly added into vigorously stirred NH_4OH solution to produce $\text{Zr}(\text{OH})_4$ and $\text{Y}(\text{OH})_3$ gelatinous coprecipitates. The pH value was maintained above 10 at all times to ensure complete precipitation. Then, the resulting gels were washed with distilled water until free of Cl^- ions examined by a AgNO_3 solution. The pounded gels and *n*-butanol were mixed together

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to produce a suspending liquid in which the gels would be dehydrated by way of azeotropes when the temperature of the mixture went up to 93 °C (azeotropic temperature). The dehydrating speed was high and *n*-butanol could be retrieved , because the water content of azeotrope was about 44.5 % (mass fraction , %) and the received azeotrope from the cooler separated *n*-butanol from water whose purity was 92.3 % . The temperature of the mixture rose to 117 °C after the residual water was completely distilled off from the gels . The distillation processing wouldn't end until keeping at 117 °C for 30 min . Then the oven-dried (at 80 °C) distillation precursors were calcined at 800 °C for 1 h to prepare the dispersed and ultrafine ZrO_2 (Y_2O_3) powders .

Differential thermal analysis (DTA) was carried out from room temperature to 1 000 °C at a heating rate of 10 °C/ min in order to study the decomposition of the as-prepared precursors . The phase transitions with the calcination temperatures were examined by XRD and IR measurements . The specific surface area and particle size were determined with BET and TEM techniques . Then the powders were dry-pressed ($d 8 \text{ mm} \times 4 \text{ mm}$) and normal-sintered (1 450 °C , 2 h) . The volume density was measured by water-draining method .

3 RESULTS AND DISCUSSION

3.1 Characterization of powders

Fig.1 shows the DTA curves for two gel precursors . For the only water-washed gels (WW) , a strong and sharp endothermic peak at 160 °C could be attributed to the dehydration of absorbed water and hydrated water ; and a sharp exothermic peak at about 430 °C resulted from the crystallization of ZrO_2 . However , for the *n*-butanol distilled precursors (AD) , the corresponding endothermic peak at 120 °C was smooth as a result of effectively dehydration by *n*-butanol distillation processing ; and the corresponding exothermic peak was not clearly seen yet because the precursors were very dispersed and porous ; and the sharp exothermic reaction at about 800 °C was related to combustion of the residual *n*-butanol .

Fig.2 shows a series of XRD patterns obtained after different thermal treatments . The gels were amorphous below 400 °C , but at 500 °C they transformed to the cubic zirconia ($c\text{-ZrO}_2$) , without other phases . Therefore the exothermic peak at 430 °C in the DTA curve was related to the crystallization temperature of ZrO_2 . The $c\text{-ZrO}_2$ peaks gradually became sharper with increasing temperature , but the monoclinic phase ($m\text{-ZrO}_2$) wasn't observed at 800 °C .

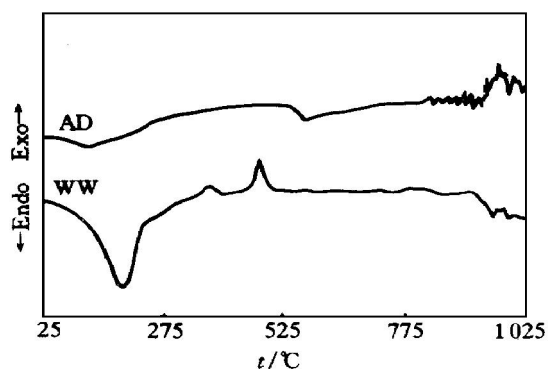


Fig.1 DTA curves of water-washed (WW) and *n*-butanol distilled (AD) precursors

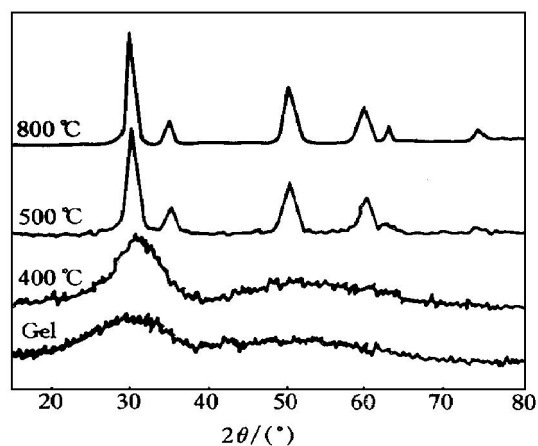


Fig.2 XRD patterns of distilled precursors at different calcination temperatures

Effects of calcination temperature on the specific surface area (S_{BET}) and average particle

size ($d = 6/(\rho \cdot S_{\text{BET}})$) of the powders are shown in Fig. 3. S_{BET} decreased greatly with increasing calcination temperatures, but the corresponding increase in the particle size especially above 800 °C was observed. For example, the specific surface area was 62 m²/g, and the average particle size was 16 nm when calcined at 800 °C for 1 h (for the only water-washed powders, they were 33 m²/g and 30 nm, respectively). So 800 °C/1 h was good calcination conditions to increase sinterability of ZrO₂ powders. Fig. 4 shows the TEM micrograph and very small particle size of the powders, without hard agglomerates.

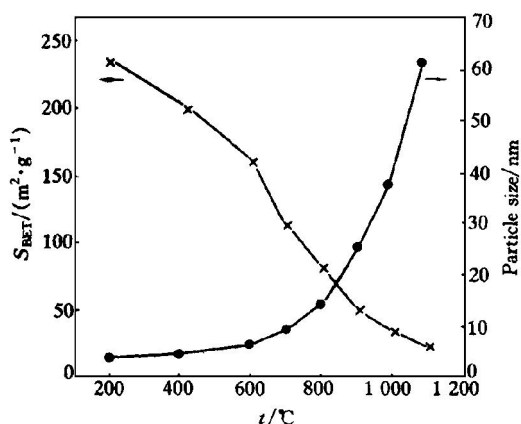


Fig. 3 Effects of calcination temperatures on specific surface area and average particle size of powders

Fig. 5 illustrates the IR spectra of the distilled precursors and calcined powders. The structure of zirconium hydroxide was most probably $[Zr_4(\mu-OH)_8(\mu_3-O)_2(H_2O)_2] \cdot xH_2O$ which was made up of absorbed water, coordinated water, bridging and nonbridging hydroxyl groups^[8]. The broad absorption bands at 3411 cm⁻¹ were due to an O-H stretch, and the three peaks at 1627, 1543 and 1373 cm⁻¹ corresponded to O-H bending. The peak at about 1000 cm⁻¹ was absorption due to chemisorbed n-butanol, i.e. C-O stretching. The removal of water from the powders calcined at 500 °C wasn't completely finished because the O-H

absorption bands didn't disappear until calcined at 800 °C. Volatilization of hydroxyl groups in crystal lattice would lead to big porosity, especially flaws in the final ceramics, so it was important to remove all hydroxyl groups.

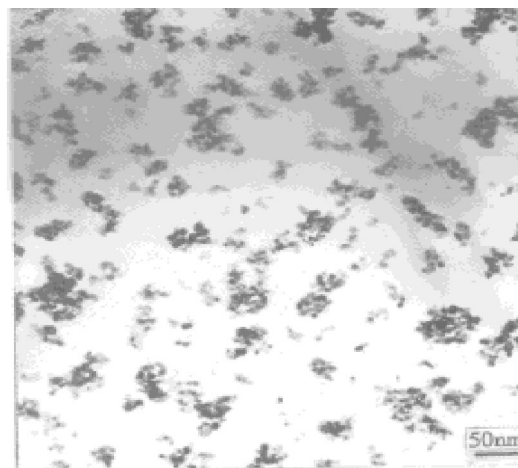


Fig. 4 TEM micrograph of the powders calcined at 800 °C for 1 h

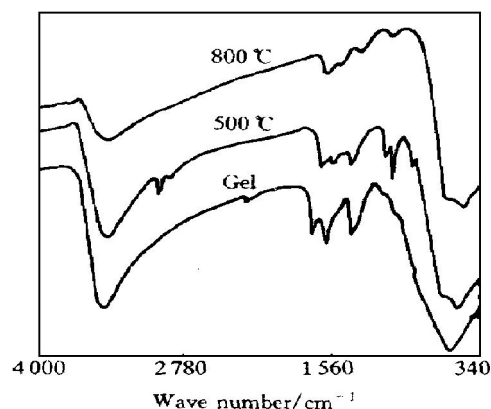


Fig. 5 IR spectra of distilled precursors and calcined powders

3.2 Sinterability

Nanometer ZrO₂-8% Y₂O₃ powders prepared by the azeotropic distillation processing were sintered to 98.5% TD at 1450 °C for 2 h, with the average grain size of 0.3 μm. Nearly complete densification at a relatively low

sintering temperature was attributed to the elimination of hard agglomerates during dehydration and calcination as a result of the removal of hydroxyl groups and water by *n*-butanol azeotropic distillation.

For the water-washed gels which contained a great deal of water, particle bridging by hydrogen bonding of water to hydroxyl groups of adjacent particles occurred. As a result, gel particles were in contact with each other. When dried, these bridging water molecules were lost, but the particles were close enough that hydrogen bonding directly occurred between terminal hydroxyl groups on the particle surface. When calcined, further dehydration led to the formation of actual chemical bonds Zr-O-Zr between the close contacting powder particles, yielding hard agglomerates. Thus, the difficult removal of porosity between agglomerates greatly lowered the density of ceramics (only 85 % TD on the same sintering conditions). However, for the azeotropic distilled precursors, there was no bridging between adjacent particles by hydrogen bonding of water because of the removal of free water and replacement of hydroxyl groups with butoxy groups. Furthermore, because of steric effects of excess *n*-butanol, the butoxy groups also acted to prevent close approach of individual particles. Third, the removal of butoxy groups didn't result in Zr-O-Zr chemical bond formation between particles. Because of these, the possibility of hard agglomerate formation during drying and calcination was effectively eliminated. As reported, if the sintering temperature fixed, the densification rate of ceramics varied inversely with the fourth power of powder particle size^[1].

So preparation of nanometer ZrO_2 (Y_2O_3) powders and elimination of hard agglomerates by the azeotropic distillation method resulted in good sinterability.

4 CONCLUSIONS

(1) Because of the removal of interparticle free water and replacement of surface hydroxyl groups with butoxy groups, the formation of Zr-O-Zr chemical bond, i.e. hard agglomerates was effectively avoided.

(2) By this method, nanometer ZrO_2 -8 % Y_2O_3 powders calcined at 800 °C for 1 h, with average particle size of 16 nm, could be sintered to 98.5 % TD at 1450 °C for 2 h with average grain size of 0.3 μm .

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