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Synthesis of 3Y–ZrO_2 nano-powders via a W/O emulsion

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Abstract

Tetragonal 3Y–ZrO_2 powders of 20–40 nm were prepared in a stable W/O emulsion system. Two variables, *P* and *G*, were used to investigate the properties of the emulsion, then the optimal parameters were determined for the production of 3Y–ZrO_2 nano-powders. The particle size and size distribution were measured, and the results showed that the quality of final powders made by emulsion is better than those prepared by the traditional coprecipitation process. The texture of dried samples and precipitates measured by TEM showed that the polymeric network can effect greatly on the quality of the final powders.

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

1. Introduction

3YSZ (stabilized zirconia with 3 mol% Y_2O_3) powder is used in many advanced structural, high-temperature and electrical ceramic applications due to its unique properties such as low thermal conductivity, high fracture toughness with a relatively high thermal expansion coefficient [1]. The investigations have led to the development of a wide variety of production techniques. Among these are conventional aqueous precipitation, hydrothermal processing, sol–gel, gas-phase reactions, and precipitation in reverse emulsion, laser vaporization, plasma process, all of which have been used in attempts to prepare various types of nanoclusters [2,3]. Emulsions as new micro-reactors for the preparation of nanophase particles are of great interest to many researchers [4,5]. By using this technique, not only the size and shape of a nanoparticle can be precisely controlled, but a controlled size distribution of particles can also be achieved [6]. There are a number of studies concerning the synthesis of nanoparticles via the emulsion method [7–10]. However, only a few of these have focused on the preparation of 3YSZ nano-powders by emulsion.

2. Experimental

For this study, octane (A.R., Beijing Chemical Co.) as the oil phase, Span-80 (A.R., Shanghai Chemical Co.) as the surfactant phase, $ZrOCl_2{\cdot}8H_2O$ (A.R., Jiaozuo General Chemical Plant), YCl_3 solution (A.R., Beijing Chemical Co.), ammonia (A.R., Beijing Chemical Co.) were used in the preparation of micro-emulsions. Before coprecipitation, each reactant, $ZrOCl_2{\cdot}8H_2O$ solution, YCl_3 solution and $NH_3{\cdot}H_2O$ solution were added to the solutions comprised of the same weight ratio of water, oil and surfactant phase separately. These were then mixed together to form a slurry of the 3YSZ precursors, $Zr(OH)_2$ and $Y(OH)_3$. After coprecipitation, the precursor was calcined to give 3YSZ powders.

In our work, SPA denotes emulsion systems where Span-80 is used as the surfactant. In order to compare the current technique with conventional coprecipitation techniques, an additional experiment was done with no surfactant or oil. This reaction system is referred to as the CCP system. All experiments were conducted at ambient pressure

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and 40 °C. Analyses were performed by using transmission electron microscope (TEM), small-angle X-ray scattering (SAXS), X-ray diffraction (XRD) and size distribution analyzer.

3. Results and discussion

3.1. Properties of emulsions

The basic conditions for an effective emulsion system for the preparation of 3YSZ nano-powders are as follows [11]:

(1) the emulsion systems must be stable,
(2) the emulsion is suitable for reaction, i.e., it has a low viscosity,
(3) the type of emulsion should be W/O, and
(4) the content of aqueous phase is sufficiently high to provide a high production rate at a low cost.

There are many factors that affect the characteristics of an emulsion and subsequently the properties of the powders [12–14]. These include the type and concentration of surfactant, the concentration of aqueous phase, the volume ratio of water to oil phase, mixing intensity and time of emulsion formation as well as, temperature and pressure. If an emulsion is unstable, large droplets tend to form from the conglomeration of small ones, thus leading to an uncontrollable size distribution of powders. Two parameters were used to express the weight ratio of oil, water and surfactant phase in the emulsion system:

$$G = W_{\text{oil}} \times \frac{100}{W_{\text{oil}} + W_{\text{sur}}} \quad (1)$$

$$P = W_{\text{wat}} \times \frac{100}{W_{\text{wat}} + W_{\text{oil}} + W_{\text{sur}}} \quad (2)$$

where W_{wat}, W_{oil} and W_{sur} are the weight of water, oil and surfactant, respectively. For the preparation of a series of emulsion systems with different P and G values, the emulsion was allowed to stand undisturbed for 1 h after stirring with an ultrasonic oscillator. The emulsion was then considered stable provided no stratification of liquid phases is formed. The stable regions for the SPA emulsions is illustrated in Fig. 1. This result is similar to Li's work [1]. It can be seen from Fig. 1 that there are two stable regions in the SPA system, one corresponding to a region with $G \leq 60$ and $P \leq 40$ and another with $G \geq 90$ and $P \leq 60$.

In our work, two emulsions with a zirconium salt or ammonia were mixed to achieve coprecipitation. Thus, it is important to mix both emulsions homogeneously for the production of a low viscosity emulsion [15]. A series of SPA emulsions with $P = 50$ and G in the range of 40–80 were thick and viscous and, hence not suitable for the reactions. Emulsions of a zirconium salt with low P and high G values were expected to result in low viscosity. For ammonia emulsions with $G = 90$, the viscosity increased to a higher

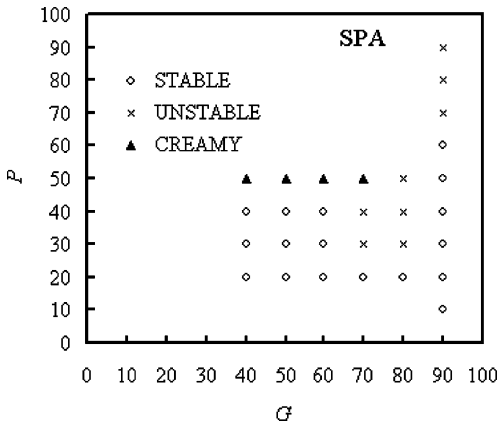

Fig. 1. Stable regions of SPA emulsion system.

value when P was increased from 40 to 50. However, the absolute value of the viscosity was not so high in the P region, from 20 to 70, with even the highest value being only about 45 cP (×10 m Pa s). It was, however, still suitable for the precipitation process.

Emulsions can be classified into water in oil (W/O) and oil in water (O/W) systems. It is desirable to have a W/O emulsion for the production of fine powders. Normally, these can be determined based on their electrical conductivity values (κ) [16]. If the oil phase is continuous in a W/O type, κ can be very small. In the SPA system, the type of ammonia emulsions with $P \leq 30$ at the point $G = 90$ are W/O. Zirconium emulsions with P regions from 10 to 50 at the point $G = 90$ are also W/O.

For both a zirconium salt emulsion and an ammonia emulsion in the SPA system, the emulsion with $G = 90$ and $P = 30$ was found to be optimal for powder productions.

3.2. Characteristics of nano-powders

3YSZ (stabilized zirconia with 3 mol% Y_2O_3) nano-powders were obtained after calcining the precursors, mixtures of $Zr(OH)_2$ and $Y(OH)_3$, at 800 °C for 3 h. The XRD data show that the main phase is tetragonal with a small amount of monoclinic phase present. Fig. 2 shows the TEM micrographs of 3YSZ nano-powders from the SPA and CCP systems. The particles obtained from SPA system are roughly spherical while those from CCP are not. The approximate grain size and the shape can be evaluated from the micrographs. To determine the average particle sizes, SAXS was performed. Of the various systems, the average particle size of SPA powder was found to be finer (~30.4 nm) while that from the CCP system is coarser (~57.6 nm).

Fig. 3 shows the size distribution of the powder agglomerates obtained from the systems measured by a size distribution analyzer. The mean sizes (D_{50}) of the agglomerates are 0.39 and 0.58 μm for the SPA and CCP systems, respectively. It is clear from Fig. 3 that the powders obtained from the SPA system has narrower size distributions and more than 80% of the agglomerates are below 1 μm. Only about

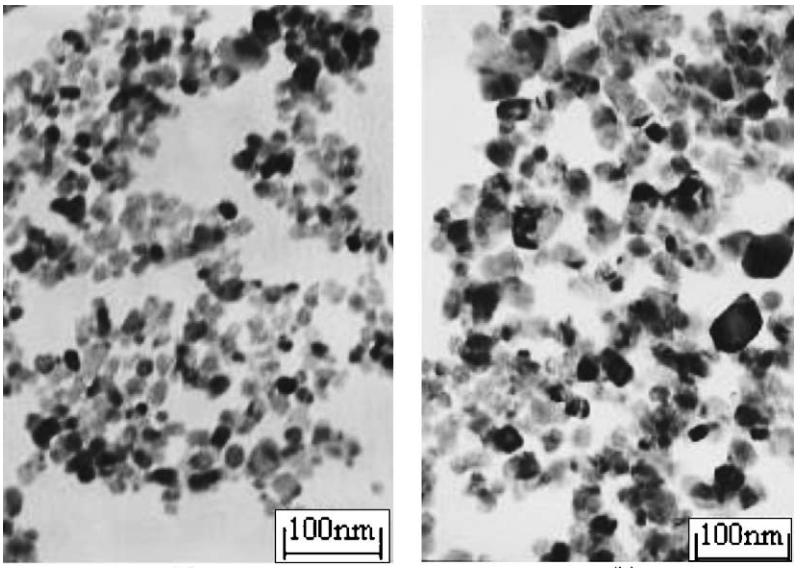

Fig. 2. TEM micrographs of 3YSZ nano-powders: (a) SPA and (b) CCP.

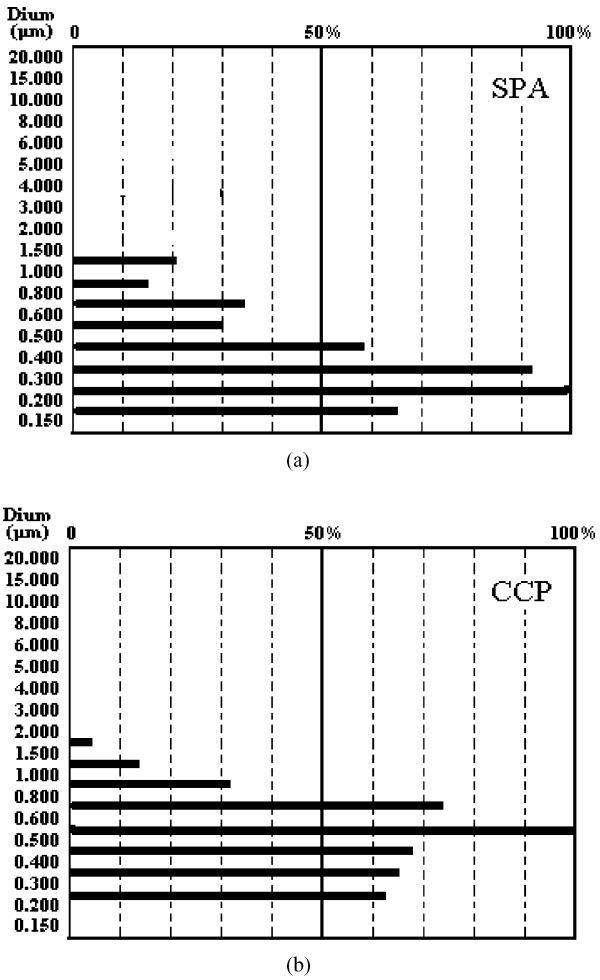

Fig. 3. The size distributions of 3YSZ nano-powders: (a) SPA and (b) CCP.

60% of those from the CCP system are below 1 μm. Based on the size and its size distribution it can be said that the SPA system has less tendency to agglomerate than that by CCP.

3.3. Polymeric network

For an ideal emulsive process, the reactant solution should be a fine emulsion of numerous droplets that are equal in size and uniform in concentration. Each droplet from one reactant solution will react individually with droplets from the other reactant solution. This enables the formation of droplets with a uniform size and shape. That is, an individual emulsion droplet serves as a reactor where nucleation and particle growth can occur [17]. Further, the presence of a network, which is formed by the surfactant and oil phase, has been found to be useful in maintaining the specific reaction environment [18].

The precipitate mixture and dried samples (<200 °C) of precursor were prepared for TEM observation. It appears from Fig. 4 that the samples from emulsion systems contain a polymeric network.

Fig. 4 shows a polymeric network in the precipitates of the SPA system and that the network is more distinct from the dried sample. However, the samples from the CCP system showed no evidence of a network. The high quality of the nano-powders from the SPA system might be attributed to the presence of polymeric network in the system.

Here the network provides a reaction environment to keep the well-distributed droplets, as well as prevents the precipitates form aggregation. However, it is well known that the biggest problem of the wet chemical methods, including emulsion methods, is agglomeration, which has a great influence on obtaining ultrafine particles with homogenous properties. In this process, there are three main ways to

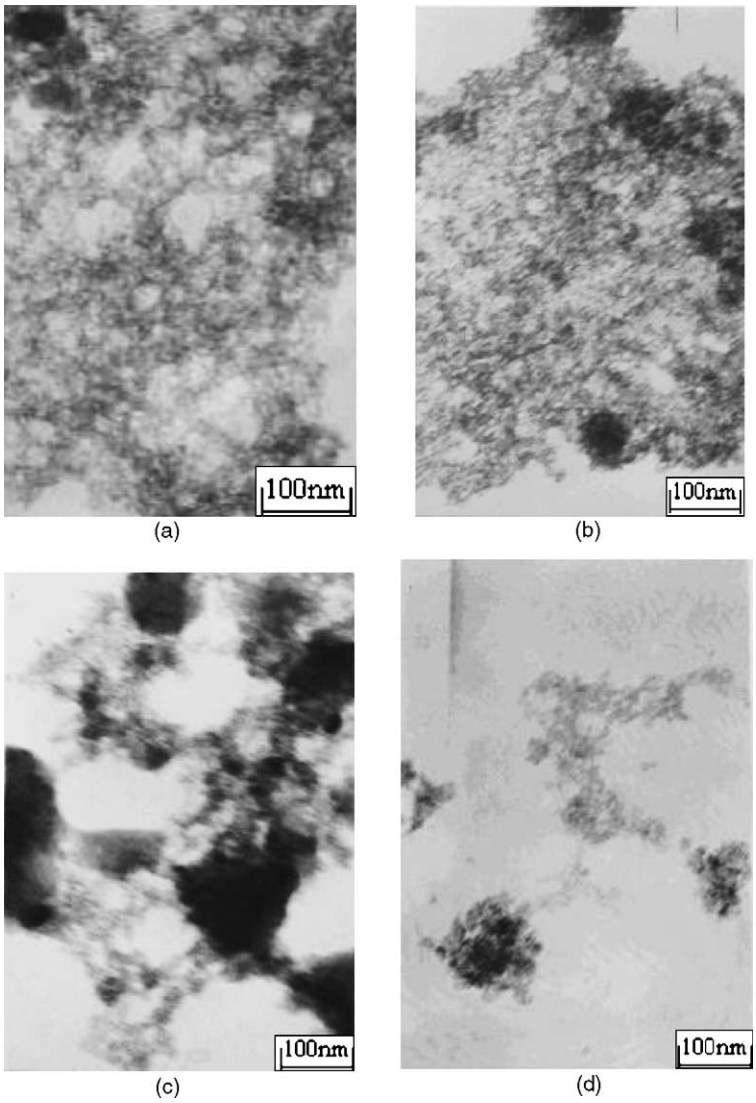

Fig. 4. TEM micrographs of amorphous precursors after drying (a) precipitate of SPA, (b) dried sample of SPA, (c) precipitate of CCP and (d) dried sample of CCP.

induce agglomeration. (1) The first one is driven by Brownian movement in the precipitation reaction stage. Two particles can form an aggregate if they have sufficient kinetic energy against the barrier stack of hindering particles from forming an aggregate via collision. This barrier stack can be expressed by [19]:

$$V_b = V_a + V_e + V_c \quad (3)$$

where V_a is the Van der Wall attractive force and is a negative value, V_e is the electrostatic repulsive force and the value of which is positive, V_c is the contribution of the shape and position from the adsorption of the organic macromolecule on the surface of the particle and the value can be positive or negative. From Eq. (1) it is clear to make V_b larger, V_a should be a smaller value, V_e a larger value, and keep V_c at a larger positive value. To meet this requirement, a suitable emulsion system is required. In our work Span-80 was used as the surfactant and octane as the oil phase. In another preparation of Ni nano-particles, the function of a polymeric network in the size, shape and agglomeration of particles was reported [11]. (2) The second process for forming an aggregate involves a separation process driven by surface tension via hydrogen bonds. In our work, a W/O type emulsion was used, and agglomeration was largely avoided in this stage. (3) The third process involves partial sintering in the calcining process. In our work, a higher temperature was used to calcine the precipitate so agglomeration caused in this stage should be considered mainly.

4. Summary and conclusions

(1) In the SPA system, for both emulsions with $G = 90$ and $P = 30$ were optimal for ZrO_2 nano-powder production.

(2) Of the two systems investigated, the particle size of SPA powder was found to be finer (30.4 nm), while that from CCP system was coarer (57.6 nm).
(3) Nano-powders of the SPA system has a more narrower size distribution and more than 80% of the agglomerates are below 1 μm. But only about 60% of those from the CCP system are below 1 μm.
(4) The high quality of the nano-powders from SPA can be attributed to the presence of a polymeric network made of surfactant and oil phase.

Acknowledgements

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