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Nano ZrO_2 (Y_2O_3) particles processing by heating of ethanol–aqueous salt solutions

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Abstract

A new method of heating a $ZrOCl_2$ and $Y(NO_3)_3$ solution with an ethanol–water mixture as a solvent was used to synthesize $ZrO_2(Y_2O_3)$ nanoparticles. The reaction mechanism, the influence of heating temperature and time on synthesizing process and final powder characteristics were investigated. It was revealed that during the heating period, the hydrolysis reaction of $Y(NO_3)_3$ was strongly suppressed and no $Y(NO_3)_3$ would precipitate. The composition of the precipitate was similar to when only $ZrOCl_2{\cdot}8H_2O$ was heated in the alcohol–aqueous solution. Only when the heating temperature was high enough that the dielectric constant decreased to <25 could precipitation occur. The higher the temperature, the shorter the time needed. The specific surface area of the powder was significantly influenced by heating time. To avoid agglomeration, heating time should be long enough to ensure complete reaction.

Keywords: ZrO_2 powders; Chemical preparation

1. Introduction

Tetragonal zirconia polycrystals stabilized by yttria (Y-TZP) have worldwide interest because of their high strength and toughness. To produce high quality Y-TZP, it is necessary for the powders to have a homogeneous composition, small grain size, narrow size distribution and low agglomeration. Several methods, such as co-precipitation [1], hydrothermal process [2] and emulsion [3] have been applied to prepare ZrO_2 powders. Recently, a new method of heating ethanol–aqueous salt solutions has been developed to synthesize nano ZrO_2 powders with good sintering ability [4–6]. When $ZrOCl_2$ solution with an ethanol-water mixture as a solvent is heated [4–8], the dielectric constant of the solution decreases significantly. As a result, the salt solution becomes supersaturated and precipitation occurs. Then, after drying and calcination, nano ZrO_2 powders could be obtained. However, up to now, most of the work was focused on the parameters such as the kind of alcohol, the addition of dispersant and the concentration of the solution.

In this work, the reaction process during the heating period and some other parameters which influence the process have been investigated.

2. Experiment

Zirconyl chloride octahydrate and yttrium nitrate were dissolved in dilute water–ethanol (volume rate = 1:5) mixture according to 97 mol% $ZrO_2 + 3$ mol% Y_2O_3 to prepare the starting solution. A specific amount of PEG was added as a dispersant. The starting solution was uniformly heated to a predicted temperature in a thermostatic bath and kept at this temperature for a certain time when the solution turned into a white gel-like precipitate. Then the NH_4OH solution was added to the precipitate and vigorously stirred untill $pH > 9$ was reached. The precipitate was washed repeatedly with distilled water for complete removal of Cl^-, dewatered by ethanol, dried at 120°C for 12 h and calcined at 600°C for 2 h. The detailed process has been described in Ref. [4]. For comparison, $ZrOCl_2$ and $Y(NO_3)_3$ were heated in a similar ethanol–aqueous solution separately.

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TEM was employed to determine the morphology and the particle size of the calcined powders. The crystalline phases of calcined powders were deduced by XRD. The effective diameter of the precipitate was determined by the laser-scattering method. The BET specific surface area of the powders was obtained by N_2 adsorption–desorption isotherms at 77 K.

3. Results and discussion

3.1. Precipitation reaction process during the heating period

An important stage of heating ethanol–aqueous salt solutions is the forming of a gel-like precipitate when the solution is heated. Although the detailed process is as yet unclear, some preliminary analysis could be taken by heating $ZrOCl_2$ and $Y(NO_3)_3$ in ethanol–aqueous solution separately.

Experiments showed that precipitation occurred when $ZrOCl_2{\cdot}8H_2O$ was heated in ethanol–aqueous solution alone. Thermal analysis to the precipitate indicate that the composition is $Zr_4O_2(OH)_8Cl_4$ [9], which means that the reaction may happen as follows:

$$4ZrOCl_2 + 6H_2O = Zr_4O_2(OH)_8Cl_4 \downarrow + 4HCl \quad (1)$$

When $Y(NO_3)_3{\cdot}6H_2O$ was heated in the ethanol–aqueous salt solution alone for 6 h, no precipitation occurred. During this period, the pH value decreased from 5.21 to 4.96, revealing that some hydrolysis reaction had happened. Calculated from the change of pH value according to the equation $Y^{3+} + 3H_2O = Y(OH)_3 + 3H^+$, only about 0.02% of the reaction had been accomplished. Obviously, this hydrolysis reaction was suppressed because of the acidic condition. Thus, no precipitation occurred.

Based on these results, it would be reasonable to say that when $ZrOCl_2{\cdot}8H_2O$ and $Y(NO_3)_3{\cdot}8H_2O$ were heated together in the ethanol–aqueous solution, the hydrolysis reaction and precipitation of $Y(NO_3)_3$ would be suppressed more strongly because of the lower pH value (about 1 or less) in the solution. The composition of the precipitate was similar to that when only $ZrOCl_2{\cdot}8H_2O$ was heated in the ethanol–aqueous solution. Without any disturbance, it is believable that the $Y(NO_3)_3$ distributed uniformly in the precipitate during this period.

This deduction could be identified indirectly by the change of the phase composition of the powders calcined at different temperatures. XRD pattern of the powders showed that the monoclinic phase decreased from 14.9 to 0.0% when the calcining temperature rose from 600 to 900°C [4]. This phenomenon was opposite to that in the powders synthesized by the common co-precipitation method [10,11] and could only be explained by the special synthesizing process as discussed above. First, when the ethanol–aqueous salt solution was heated, the hydrolysis reaction of $ZrOCl_2{\cdot}8H_2O$ occured as shown in Eq. (1) and formed a gel-like precipitate. At this stage, $Y(NO_3)_3$ was distributed homogeneously in this gel-like precipitate. Then, after NH_4OH was added, the precipitate turned into $Zr(OH)_4$, $Y(NO_3)_3$ turned into $Y(OH)_3$ and still distributed in the $Zr(OH)_4$ homogeneously. At last, $Zr(OH)_4$ was dehydrated to become ZrO_2 after calcination, $Y(OH)_3$ turned into Y_2O_3 and infiltrated into ZrO_2 particles, so the ZrO_2 particles turned from monoclinic phase to tetragonal phase. Certainly, the higher the calcining temperature, the easier the infiltrating. That is why the tetragonal phase content increases with the temperate rising.

3.2. Influence of heating temperature on the reaction process

The heating temperature has an obvious influence on the precipitation process. When the temperature was too low, no precipitation occurred. With the temperature rising, the time for precipitation occurring shortened rapidly, when the temperature rose to 80°C, only 2 min was needed. This phenomenon could be explained by the change of dielectric constant of the solution. Fig. 1 shows the relationship of dielectric constant with heating temperature [7]. It can be seen that the dielectric constant decreased rapidly with increasing temperature. Since the decrease of the solvent dielectric constant would result in the decrease of the solubility of an inorganic salt [7], precipitation would occur more easily at higher temperatures. Detailed experiments showed that the dielectric constant was about 25 when the precipitation began to occur, which was similar with the results obtained from 2-propanol-aqueous solution [7].

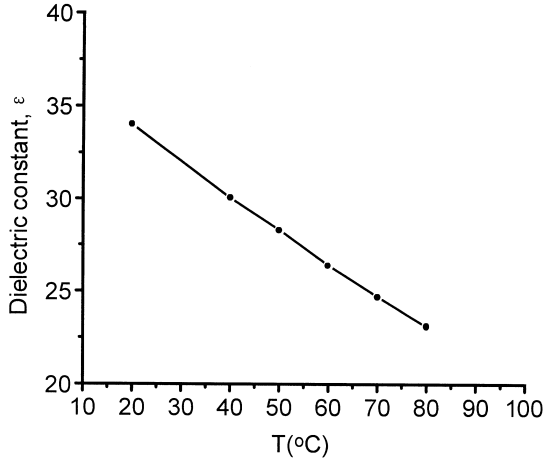

Fig. 1. Relationship of dielectric constant with temperature.

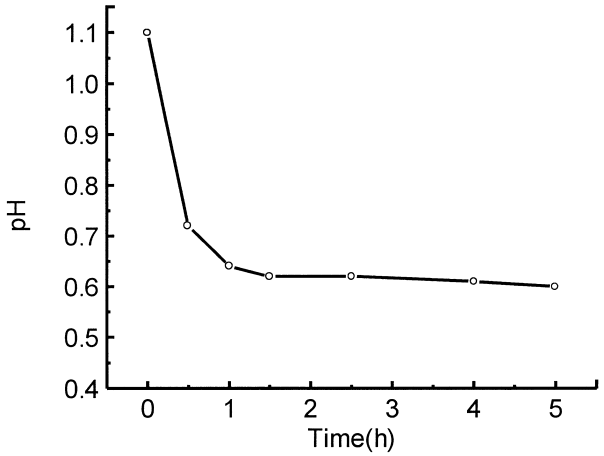

Fig. 2. Changing of pH value with heating time.

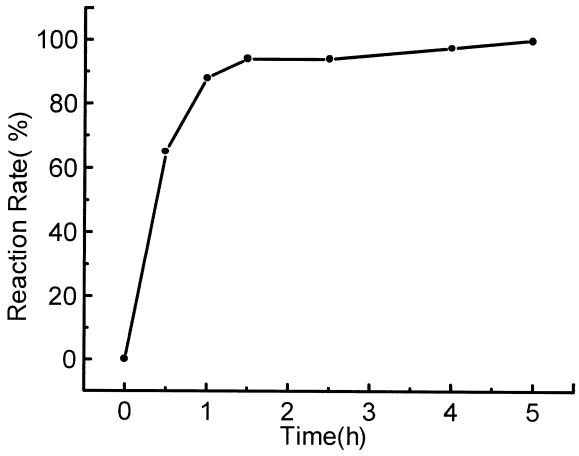

Fig. 3. Reaction ratio of $ZrOCl_2$ with time.

3.3. The influence of heating time on the reaction process

Fig. 2 shows the change of pH value with the heating time. During the first 1.5 h, the pH value decreased obviously. One and a half hours later, the decreasing speed slowed down, which indicated that the reaction had attained a balance after 1.5 h. Fig. 3 is the reaction ratio calculated according to Fig. 2 and Eq. (1), the reaction ratio reached above 94% after 1.5 h. Though $ZrOCl_2$ could be hydrolyzed in water when no alcohol was added and the reaction ratio could be as high as 99%, the time needed might be as long as tens or hundreds of hours [12]. Obviously, the reaction speed is much higher in the ethanol–aqueous solution.

Although the heating time has little influence on the particle size, it has an apparent influence on the specific surface area. The specific surface area of powders heated for 5 h was 66 m^2/g, much larger than that heated for 1 h, which was only 46 m^2/g. This result was coincident with the result obtained by the laser-scattering method, which showed the effective diameter of the precipitate heated for 5 h (about 316 nm) was much smaller than that of heated for 1 h (about 586 nm). Since the effective diameter always represents the size of agglomerates in the solution [13], that result meant that the agglomerates decreased with the heating time. The possible reason for this phenomenon is based on the reaction mechanism. As discussed in Section 3.2, when the ethanol–aqueous salt solution was heated, precipitation occurred because of the reaction shown in Eq. (1). However, if the heating time was too short (1 h), only about 88% of the reaction could be finished according to Eq. (1) (not taking the core forming and grain growth into account). If ammonia was added at this time, another kind of precipitation would begin because the ammonia would react with $ZrOCl_2$ quickly. As this kind of precipitation happened rapidly and inhomogeneously, it was very easy to form agglomerates. However, when the heating time lasted for 5 h, the reaction was almost completed (the reaction ratio was about 99.5% after heating for 5 h) and the precipitate was formed homogeneously. The ammonia could only changed the pH value but could not change the uniformity of the precipitation. So, there were little agglomerates formed.

4. Conclusions

1. When $ZrOCl_2$ and $Y(NO_3)_3$ were heated together in the ethanol–aqueous solution, the hydrolysis reaction of $Y(NO_3)_3$ was strongly suppressed and would not precipitate, the composition of the precipitate was similar to that when only $ZrOCl_2{\cdot}8H_2O$ was heated in the alcohol-aqueous solution.
2. Time for the precipitate to occur shortened rapidly with the rising of the heating temperature. Only when the reaction temperate was high enough that the dielectric constant decreased to <25 could the precipitation occur.
3. The agglomeration of the powders is obvious if the heating time is too short. To avoid agglomeration, reaction time should be long enough to ensure the solution react complete.

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