Materials

Effect of particle size on phase structure of ZrO_2 produced by hydrolysis of $ZrOCl_2$ solution

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Abstract: A method to produce ZrO_2 nano-particles is developed and the effect of particle size on the phase structure of ZrO_2 is studied. The method is based on the hydrolysis of $ZrOCl_2$ solution in the reverse micelles of a liquid-liquid two-phase system, in which AOT (sodium 2-ethylhexyl sulfosuccinite) and toluene are chosen as the surfactant and organic phase, respectively. The reverse micelles prevent the aggregation of primary particles, the nano-particle size increases as the AOT content decreases. The TEM, XRD and particle-size analysis results show that the occurrence of metastable tetragonal ZrO_2 is attributed to the effect of the particle size other than the effect of the crystallite size. The ratio of t-phase to m-phase increases as the particle size decreases, and 28 nm is the critical size for t-phase to m-phase transformation.

Key words: zirconia; nano-particles; hydrolysis; phase transformation

1 Introduction

Tetragonal zirconia polycrystals (TZP) is an important structural ceramic with excellent mechanical properties. Zirconia (ZrO_2) is also a useful catalysis or an important support material for catalysis. Many methods have been explored in order to get superfine ZrO_2 powders, such as hydrothermal process, vapor phase hydrolysis, gas condensation, sol-gel process, and combustion methods [1-2]. Matsui and Ohgai reported the formation mechanism of hydrous-ZrO_2 particles produced by the hydrolysis of $ZrOCl_2$ aqueous solution [3-4]. In previous reports [5], we added carbon nanotubes (CNTs) in the hydrolytic process of $ZrO(NO_3)_2$, and ZrO_2 powder with nanometers was obtained.

The reverse micelles method is a promising technology to produce nano-particles [6-7]. The aqueous solutions immiscible with oil will form very small mono-dispersed droplets in the organic phase by adding a certain surfactant, in this case the aqueous droplets form nanometer size particles with spherical shape in the surfactant/oil/aqueous solution systems. When these droplets disperse in reserved micelles, mono-disperse colloidal particles will be synthesized. Using this method, it is possible to avoid the aggregation of particles, which is a key problem for other methods of producing nano-particles. In this paper, a new method is developed to produce ZrO_2 nano-particles *via* the hydrolysis of $ZrOCl_2$ solution in the

reverse micelles of a liquid-liquid two-phase system.

ZrO_2 has three polymorphs: monoclinic (m-phase, below 1170°C), tetragonal (t-phase, between 1170 and 2370) and cubic (c-phase, above 2370°C). The high temperature t-phase and c-phase, which have much better mechanical properties and high ionic conductivity, can be stabilized to room temperature by adding some dopants [8]. The occurrence of metastable t-phase ZrO_2 as a crystallite size effect was reviewed by Garive [9]: the stabilization of t-phase at low temperatures was due to the lower surface free energy, and the critical crystallite size was 30 nm below which the m-phase will transform to t-phase. Srinivasan [10] criticized the concept of crystallite effect and pointed out that the X-ray crystallite size may not be a validity measure on the role of surface energy in the stabilization of t-phase. Therefore, in this paper, TEM (transmission electron microscopy), XRD (X-ray diffraction) and particle-size analysis were applied on the studies of the effect of particle size and crystallite size on the phase structures of ZrO_2 particles.

2 Experiment procedure

The ZrO_2 nano-particles were produced by the hydrolysis of $ZrOCl_2$ solution in reverse micelles of a liquid-liquid two-phase system, in which AOT (sodium 2-ethylhexyl sulfosuccinite) and toluene were chosen as the surfactant and organic phase, respectively. By changing the content of AOT, different

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sizes of ZrO_2 nano-particles were produced.

(1) Sample A. (I) 0.5 mol/L $ZrOCl_2$ aqueous solution 20 mL was produced, 0.12 g AOT was added into 130 mL toluene, then these two kinds of solutions were mixed under rapid stirring at the azeotropic point (85°C); (II) After toluene and hydrochloric acid were extracted, the residue product was dried in air at 110°C to volatilize all the toluene; (III) The product at 600°C for 2 h under Ar atmosphere was sintered; (IV) The product was sintered at 700°C in air for 1 h to remove the residue sulfur element.

(2) Sample B. The producing process was just like that of sample A, only the AOT addition was increased to 0.30 g. When the AOT addition increased to 0.45 g, sample C was produced.

The nano-particles were characterized using TEM (H-800) and SEM (AMRAY-1910). The particle structure was investigated with a Siemens D5000 X-ray diffraction system with Cu K_α radiation. Delsa 440sx particle analysis apparatus was used to measure the size distribution of the particles.

3 Results and discussion

The ZrO_2 nano-particles were prepared based on the azeotropic process of a mutually non-soluble liquid-liquid system, which consisted of organic phase and aqueous phase. Toluene is chosen as organic phase because it has a higher boiling point that is propitious to the escape of aqueous phase from the liquid-liquid system.

The vapor pressures of toluene and water are given as a function of temperature by the Antoine equation [11]:

$$\ln P_{vp} = A - \frac{B}{C+T} \tag{1}$$

where P_{vp} is the vapor pressure of pure-component in millimeters of mercury and T the temperature, K. The Antoine vapor-pressure-equation coefficients, A, B and C, are listed in table 1, where M is the molar mass and ρ the density of the liquid.

Table 1 Constants of equations (1) and (4)

Phase	M	ρ / (g·cm⁻³)	A	B	C
Toluene	92.141	0.867	16.0137	3096.52	−53.67
Water	18.015	0.998	18.3036	3816.44	−46.13

For each binary system the total pressure P is given by:

$$P = \sum_{i=1}^{2} x_i \gamma_i P_{vpi} \exp\frac{\left(V_i^L - B_{ii}\right)\left(P - P_{vpi}\right)}{RT} \tag{2}$$

where γ_i is the activity coefficient of component i in the liquid mixture, V_i^L the molar volume of pure liquid i and B_{ii} the second viral coefficient of pure liquid i.

Since water and toluene are immiscible, equation (2) can be simplified:

$$P = \sum_{i=1}^{2} x_i P_{vpi} \tag{3}$$

Combining equations (3) and (1), the binary phase diagram of the toluene/water immiscible liquid system is obtained. As shown in **figure 1**, the azeotropic point is slightly below 85°C in this system. When the temperature is higher than 85°C, the components of residual liquid phase will be determined by the toluene content. The critical content of toluene is about 0.45, below which water will be remained and above which toluene will be remained. Therefore the optimized volume ratio of aqueous solution to organic phase is required.

The mole ratio of toluene to water ($n_{C_7H_8} : n_{H_2O}$) is

0.8:1 by the critical content. The critical volume ratio of aqueous solution to organic phase was calculated by the following equation with M and ρ given in table 1.

$$\frac{V_{C_7H_8}}{V_{H_2O}} = \frac{M_{C_7H_8}}{M_{H_2O}} \cdot \frac{n_{C_7H_8}}{n_{H_2O}} \cdot \frac{\rho_{H_2O}}{\rho_{C_7H_8}} \tag{4}$$
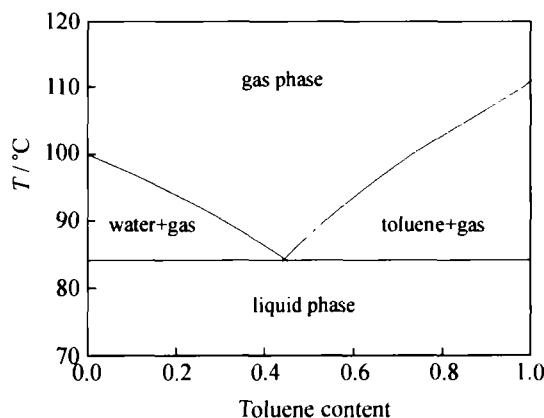

Figure 1 Binary phase diagram of the toluene/water immiscible liquid system.

By calculation from equation (4), the critical volume ratio is 4.71, so all the aqueous phase can be extracted during distillation when $V_{C_7H_8}/V_{H_2O}$ exceeds the critical value. In this experiment the ratio was chosen as 5.5, since the residual toluene was propitious to

the formation of the reversed micelle sol.

The hydrolysis reaction is:

$$ZrOCl_2 + (n+1)H_2O = ZrO_2 \cdot nH_2O + 2HCl \qquad (5)$$
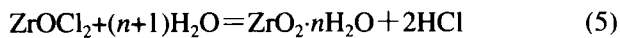
Since hydrochloride is a mutual solvent to aqueous phase, the hydrolysis reaction can be carried out when water evaporating. AOT solubilizes a large quantity of water in hydrophobic organic solvents and forms reversed micelles. The water/organic micro-emulsion system with AOT provides a medium for the hydrolysis reaction. The micelle size is determined by the ratio of solubilized water molecules to AOT molecules. During the hydrolysis process with water molecules decreasing, the micelle size is reducing. After the reaction had terminated, the primary particles of hydrous ZrO_2 were formed and solubilized by AOT in organic solvents. The primary particle size is determined by the ratio of solubilized hydrous ZrO_2 molecules to AOT molecules, so it can be controlled by the accommodation of AOT content.

Unlike the particles produced by Koji Matsui's method [3], in this paper, the primary particles were packaged in separate reverse micelles formed by AOT in toluene. Koji Matsui pointed that the primary particles of hydrous ZrO_2 must aggregate because of the strong interaction among the particles through the reaction process of hydrolysis. The AOT surrounding the primary particles formed a barrier layer and prevented the aggregation. It is considered that hydrolysis reaction ended when the transparent liquid appeared in colloidal solution. After all the toluene volatized, the sol made up of the reverse micelles containing hydrous ZrO_2 was obtained. In the drying and sintering process, the hydrous ZrO_2 transformed to ZrO_2 and further crystallized was limit in the micelle. After the elimination of the surfactant residue on the surface of particles, pure ZrO_2 powders were obtained.

The size distribution of ZrO_2 nano-particles is shown in **figure 2**, the size increases with the AOT
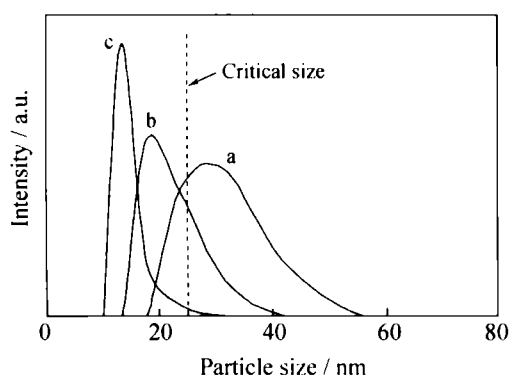
Figure 2   Particle size distribution and critical particle size: a—sample A; b—sample B; c—sample C.

content increasing, the size can be controlled by changing the AOT content. **Figure 3** is the SEM image of sample B.
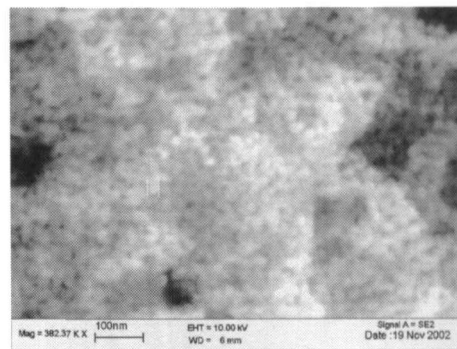
Figure 3   SEM image of sample B.

The microstructures and the XRD patterns of the powders prepared under different conditions are shown in **figure 4**, it indicates that the ratio of m-phase to t-phase decreases as the particle size decreasing. The crystallite size is calculated using the Debye-Scherrer equation:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \qquad (6)$$

where D is the crystallite size, λ the wavelength of Cu K_α radiation, β the corrected peak width in the radians calculated from $\beta = \sqrt{B^2 - b^2}$ (B is the observed peak width and b the instrumental broadening), and θ the Bragg diffraction angle.

It is postulated that the instrumental broadening is constant in the same XRD pattern. **Table 2** is the crystallite size (D) of samples A, B and C, which are calculated by formula (6) according to some parameters in the XRD data.

Table 2 indicates that the crystallite sizes had no obvious difference between t-phase and m-phase, and all the crystallite sizes for the three samples are smaller than 30 nm, but they display different phases. The results cast doubt upon the concept of a crystallite size effect on the stabilization of the tetragonal structure at low temperatures. When the particle reaches nano-scale, surface energy will play an important role in determining its phase. Using Garvie's theory [7], the critical size for m-t transformation is about 28 nm.

$$d_c = \frac{-6(\sigma' - \sigma)}{q(1 - T/T_b)} \qquad (7)$$

where d_c is the critical size, q the heat of transformation/unit volume of an infinite crystal, σ the surface free energy of the crystal, and T_b the transformation temperature of an infinite crystal.

From curve a in figure 2, the particle sizes always

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distribute in a range with a certain width. Most particles of sample A are larger than the critical size, and a few less than the critical size, as a result the structure of most crystals is m-phase. In curve b most particles of sample B are less than the critical size, and a few

larger than the critical size, and the ratio of the former to the later is consistent with the ratio of t-phase to m-phase. In curve c, most particles of sample C distribute far less than the critical size, and the dominant phase structure is t-phase.
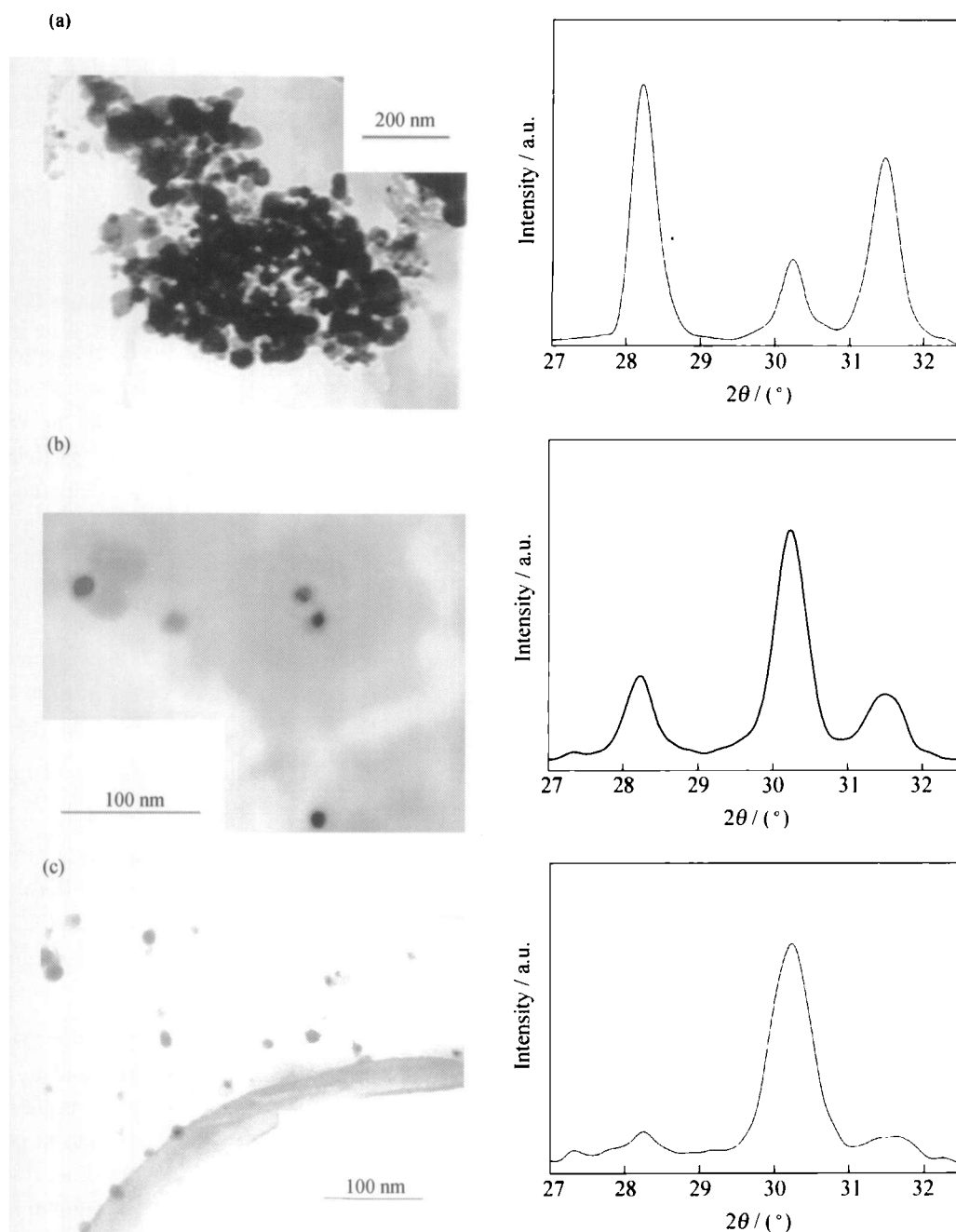

Figure 4 XRD patterns and TEM photographs of different particles: (a) sample A; (b) sample B; (c) sample C.

Table 2 Crystallite size of samples A, B and C   nm

Sample	A	B	C
$D_{(101)}$ of t(101)	25.23	20.45	18.43
$D_{(\bar{1}11)}$ of m($\bar{1}11$)	27.12	21.26	—

It can be concluded that the occurrence of tetragonal in ZrO_2 depends not on the crystallite size but on the particle size, and t-ZrO_2 is more stable than m-phase when the particle size is below 28 nm.

4 Conclusions

The ZrO_2 nano-particles were produced by the hydrolysis of $ZrOCl_2$ solution in the reverse micelles of a

liquid-liquid two-phase system, in which AOT and toluene were chosen as the surfactant and organic phase, respectively. The optimum ratio of toluene to $ZrOCl_2$ solution is more than 5 after calculation according to the binary phase diagram of a toluene/water immiscible liquid system. The reverse micelles can prevent the aggregation of primary particles, and the nano-particle size can be controlled by changing the content of AOT. The microstructures and XRD patterns of the powders show that the occurrence of metastable t-phase ZrO_2 is attributed to the effect of the particle size other than the effect of the crystallite size. The ratio of t-phase to m-phase increases as the particle size decreases, and 28 nm is the critical size for t-phase to m-phase transformation.

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