Crystallization of Titania in Methanol, n-Hexane and Water at High Temperatures

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Amorphous TiO_2 was prepared by dissolving TiCl_4 to $\text{NH}_4\text{OH}-\text{CH}_3\text{OH}-\text{H}_2\text{O}$ mixed solution and hydrolysis of titanium(IV) tetraisopropoxide. Microcrystalline anatase was fabricated by crystallizing amorphous TiO_2 gels in methanol, n-hexane and water at $120\sim 200^\circ\text{C}$ which were much lower than the crystallization temperature in air. The crystallization behavior could be adequately described by the surface chemical reaction controlled shrinking core model. Crystallization in water was much faster than in methanol and n-hexane, but the sinterability of powder prepared in water was poorer than of that prepared in organic solvents. The addition of requisite amounts of water to organic solvents was found useful in promoting crystallization of gel without loss of powder sinterability.

[titania, crystallization, high temperature, organic solvent, sinterability]

1. Introduction

Titania has been widely used as white pigment, abrasive, cosmetics, UV light protective reagent and catalyst, etc. Titania is also used as catalyst carrier because of its good mechanical properties, inertness and its low price[1-2]. In order to improve the properties of ceramics, there has been a long-term trend toward the use of finer powders[3]. It is known that organic solvents play important roles for preventing hard agglomerate formation and crystal growth during crystallization, and hard agglomeration caused by the liquid-vapor interfacial capillary force is effectively avoided by supercritical drying [4-7]. In previous papers [8-10] it was reported that CeO_2 - ZrO_2 powders crystallized in methanol and dried by supercritical drying possessed excellent sinterability than those fabricated by hydrothermal crystallization and/or calcination in air. The details of crystallization of ceramic powder in organic solvents, however, has not been clarified. In the present study, ultrafine titania powders were prepared by crystallizing amorphous gel precursor in various liquid media, such as water, methanol, and n-hexane at $120\sim 200^\circ\text{C}$. The crystallization behaviors of TiO_2 gel were described in details.

2. Experimental procedures

Amorphous TiO_2 gel was prepared by two kinds of methods. One was prepared by slowly adding 500 cm^3 of methanol solution dissolving 0.66 mol of TiCl_4 to the mixed solution of 300 cm^3 of NH_4OH (29wt.-%) - 500 cm^3 of methanol- 700 cm^3 of H_2O at room temperature. Another was prepared by hydrolysis of titanium(IV) tetraisopropoxide, i.e., 0.5 mol of $\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4$ contained iso-propanol solution was slowly added into 36 cm^3 of H_2O - 464 cm^3 of iso-propanol mixed solution. The gels were successively washed with 50 vol.-% water-50 vol.-% methanol mixed solution and methanol, and dried at room temperature using a vacuum desiccator. In order to investigate the crystallization behaviour 0.5 g of amorphous gels were heated in 6 cm^3 of methanol, n-hexane, and/or water at various temperatures for desired times. The crystallization fraction x was determined using the integral intensity of differential thermal analysis (DTA) peak corresponding to a crystallization as

$$x = (I_0 - I_1) / I_0 \quad (1)$$

where I_0 and I_1 are the DTA peak intensities of the gels before and after heat treatment, respectively. The powders used for sintering were prepared in methanol-water mixed solution at 200°C for 3 h using an autoclave with an internal volume of 100 cm^3 and dried at 300°C in air. Compacts were uniaxially pressed at 20 MNm^{-2} before cold isostatically pressing at 200 MNm^{-2} and were then sintered in air at $800\sim 1000^\circ\text{C}$ for 5 h. The phase constitution of crystallized powders and sintered compacts were determined by X-ray diffraction analysis (XRD) using Ni-filtered $\text{CuK}\alpha$ radiation. Density of the sintered body was determined by Archimedes technique. The fracture strength was determined by 3-point bending test.

3. Results and discussion

The amount of water in the dried gel was determined as 30 wt.-% by thermogravimetry indicated that the chemical composition of the gel may be describe as $\text{Ti}(\text{OH})_4$. Figs.1 and 2 show X-ray diffraction and differential thermal analysis profiles for TiO_2 gels before and after heat treatment in methanol and water at 170°C for 3 h. The starting gels were amorphous by XRD. The sharp exothermic peak observed at 370°C or 407°C is attributed to the onset of crystallization from amorphous to anatase. The crystallization temperature of the gel prepared from TiCl_4 is 37°C lower than from the hydrolysis of $\text{Ti}(\text{i-C}_3\text{H}_7\text{O})_4$. The gels

Fig. 1. XRD profiles of gels prepared from (a) TiCl_4 , (b) $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$ and heat treated (a) in (c) methanol, (d) water at 170°C for 3 h.

Fig. 2. DTA profiles of gels prepared from (a) TiCl_4 , (b) $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$ and heat treated (a) in (c) methanol, (d) water at 170°C for 3 h.

heated in methanol or water for 3 h, even at a low temperature such as 170°C , showed XRD peaks identified as anatase, and DTA peak around 370°C or 407°C disappeared indicating that the gels had crystallized to anatase completely.

Time dependence of crystallization fraction, x , and relationship between $1-(1-x)^{1/3}$ and time of gels in n-hexane at various temperatures are shown in Fig. 3. The crystallization occurred significantly above 120°C and was greatly promoted with increasing temperature. The kinetic data could adequately be described by the surface chemical reaction controlled shrinking core model[11] expressed by equation (2).

Fig. 3. (a) Time dependence and crystallization fraction, x , and (b) relationship between $1-(1-x)^{1/3}$ and time in n-hexane. Temperature ($^\circ\text{C}$); $\bullet$:120, $\square$:130, $\blacklozenge$:140, $\circ$:150

Fig. 4. Arrhenius plots of crystallization rate constants.

$\square$: in methanol, $\blacktriangle$: in n-hexane, $\blacksquare$: in water,

Fig. 5. Distributions of agglomerated particles size of TiO_2 crystallized in methanol and in water at 200°C for 3 h.

$$1 - (1 - x)^{1/3} = kt \quad (2)$$

where k , x , and t are apparent rate constant, crystallization fraction, and time, respectively.

The kinetic data of methanol and water system could also be expressed by above equation well. Arrhenius plots of the rate constants are shown in Fig.4, giving activation energies of 206, 88.0 and 89.1 kJ mol^{-1} in methanol, n-hexane and water, respectively. The crystallization rate was in the order in methanol $<$ in n-hexane $<$ in water. The activation energies in n-hexane and water were almost the same and that in methanol significantly larger. In a previous paper[9] similar results were obtained for the crystallization of ceria-doped zirconia, it was suggested that

water is entirely distributed in methanol but concentrated around the gel particle in n-hexane. Therefore, the crystallization behaviour in n-hexane is suspected to be similar to that in water, but not that in methanol. Water is essential for the crystallization of the gel and that the crystallization proceeded via a dissolution-precipitation mechanism, where the gel dissolves as hydrated ions by reaction with water adsorbed on the surface.

Agglomerated particle size distribution profiles of the powders crystallized in methanol and water are shown in Fig. 5. Average crystallite sizes of the powders crystallized in methanol and water were 7.2 and 12.7 nm, respectively, which were determined by TEM photographs. On the other hand, about 55 vol% of the powders crystallized in methanol and water consisted of agglomerated particles of 2-3 and 3-4 μm and the average agglomerated particles sizes were 2.3 and 3.7 μm , respectively.

BET specific surface area of titania powders crystallized in solvent at 200°C for 3 h and relative densities of their sintering compacts sintered at 800-1000°C for 5 h are shown in Fig. 6 as a function of water volume fraction in water-methanol mixed solution. The specific surface area increased from 62.7 to 76.9 m^2g^{-1} and grain size decreased with increasing methanol content.

Fig. 6. (a) BET specific surface area of titania powders crystallized in solvent at 200°C for 3 h and (b) relative densities of their sintering compacts sintered at 800-1000°C for 5 h as a function of water content of solution.

The titania powders crystallized in methanol at 200°C for 3 h possessed fine and narrow distribution of size, soft agglomeration and excellent sinterability, and could be sintered to 98.8 % theoretical density at 800°C, but the density decreased to 94.2 % at 900 and 1000°C. It may be due to large volume shrinkage accompanying with the anatase to rutile phase transformation. The compacts sintered at 800°C mainly consisted of anatase and those sintered at 1000°C fully rutile. The addition of 20 vol.-% water showed no significant effect on the density, but the density decreased with increasing water volume content above 50 vol.-%.

The specimens sintered at 800-1000°C showed almost the same fracture strength which showed in Fig. 7. The fracture strength also decreased with increasing water content especially above 50 vol.-%.

These results suggested that methanol is useful to depress crystal growth and powder agglomeration during crystallization. From the results shown in Figs. 6 and 7, it may be concluded that addition of a requisite amount of water to organic solvent,

Fig. 7. 3-point bend strength of TiO_2 compacts sintered at 800 (○), 900 (□) and 1000°C (◇) for 5 h using the powders crystallized in methanol at 200°C for 3 h, as a function of water content of solution.

less than 50 vol.-% in methanol, the crystallized powders possessed fine particles size, excellent sinterability and mechanical properties.

4. Conclusion

1. The crystallization of TiO_2 gel in liquid media occurred significantly above 120°C, and the gel could be completely crystallized below 200°C which was much lower than the crystallization temperature in air.
2. The crystallization data in liquid media could be adequately described by the surface chemical reaction controlled shrinking core model. Crystallization rate in water was much faster than in n-hexane and methanol.
3. By adding requisite amounts of water to organic solvents, the crystallized powders possessed fine particles size, excellent sinterability and mechanical properties.

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