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Preparation of monodispersed Y-doped ZrO_2 powders

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3 mol % Y-doped ZrO_2 powders prepared by the controlled hydrolysis of metal alkoxides were monodispersed and grown to 0.5 μm after 5 h ageing. The as-prepared powder was amorphous and hydrate but transformed into a tetragonal single phase by heating. Furthermore, the Y_2O_3 concentration of each particle was almost the same in all particles. The synthesis conditions such as ageing time, ageing temperature and water concentration greatly affected the particle morphology. The refluxing of the alkoxide solution was particularly necessary to prepare the monodispersed particles. On the basis of the variation of size distribution with ageing time, the mechanism of particle growth was discussed.

1. Introduction

One of the most promising methods for the preparation of ceramic powders is the controlled hydrolysis of metal alkoxide. This method was at first used to synthesize monodispersed SiO_2 fine particles [1, 2] and then applied to the preparation of monodispersed fine particles of TiO_2 [3, 4], Ta_2O_5 [5], ZrO_2 [6, 7], etc. As a result of these studies, the synthesis of simple metal oxide powders containing only one metal element is considerably easier. The synthesis of other element-doped oxide powders and double oxides containing two or more different kinds of metal elements has been done [6, 8] but they are more difficult because of the difference of hydration rate of each metal alkoxide. There are difficulties in finding a common alcohol to solve different kinds of metal alkoxides and make the solution homogeneous.

Fegley *et al.* [9] reported the precipitation of Y-doped ZrO_2 particles which contained about 5 and 8.6 mol % Y_2O_3 by hydrolysis of alkoxides. The powders had a fairly narrow size distribution but were not so spherical. The as-prepared powder was amorphous and with heating it transformed into a mixture of non-transformable tetragonal and cubic phases.

Y-doped ZrO_2 which consists of a meta-stable tetragonal phase is known as tetragonal zirconia polycrystalline, TZP [10]. TZP has high strength and toughness because of its micro-crack stop mechanisms, such as the transformation of the tetragonal phase into a monoclinic one accompanying the volume increase. For this reason, TZP requires a transformable tetragonal phase and its Y_2O_3 content is 2 to 4 mol % [11].

However, when the grain size of TZP increases, the tetragonal phase transforms spontaneously to a monoclinic phase. Therefore, large grain TZP has lower strength and toughness [11, 12]. Thus monodispersed fine particles of tetragonal ZrO_2 are required as the raw materials for TZP.

The purposes of the present study is firstly to prepare monodispersed ZrO_2 powders which contain 3 mol % Y_2O_3, and secondly to establish the relation of preparation conditions and particle morphology. Further, the chemical and physical properties of the powders, especially Y_2O_3 dopant concentration in each particle, are measured, and their crystallinity is studied by X-ray diffraction.

2. Experimental procedure

Zirconium-tetra-butoxide, $Zr(OC_4H_9)_4$ was dissolved in ethanol with a magnetic stirrer. Yttrium-tri-*iso*-propoxide, $Y(i\text{-}OC_3H_7)_3$ was dissolved into the $Zr(OC_4H_9)_4$–ethanol solution by ultrasonic dispersion. Because the homogeneous solution of $Zr(OC_4H_8)_4$ and $Y(i\text{-}OC_3H_7)_3$ had not been obtained just by mixing, the mixed solution was refluxed for 4 h at 74° C and became clear. The water–ethanol solution was added to the refluxed solution to hydrolyse the alkoxides.

The ethanol solution containing alkoxides and water was aged in a water bath at given temperatures from 30 to 80° C. The solution became white in a few minutes due to the formation of small particles, and further aged to make particle growth. The total ageing time was chosen from 1 to 10 h. Subsequently, the particles were centrifugally separated from the solvent and dried at 60° C in air. Some of the powders were redispersed in a basic aqueous solution and gravimetrically sedimented for a week.

The concentrations of $Zr(OC_4H_9)_4$ and $Y(i\text{-}OC_3H_7)_3$ were 0.097 and 0.006 mol l^{-1}, respectively, and were kept constant in this experiment. On the other hand, the water concentration was changed in the range of 0.10 to 0.40 mol l^{-1}. All the values of the concentrations described above were calculated on the basis of total amount of solution.

The size and shape of particles were determined with a scanning electron microscope, SEM (JEOL Ltd, Japan) and a transmission electron microscope,

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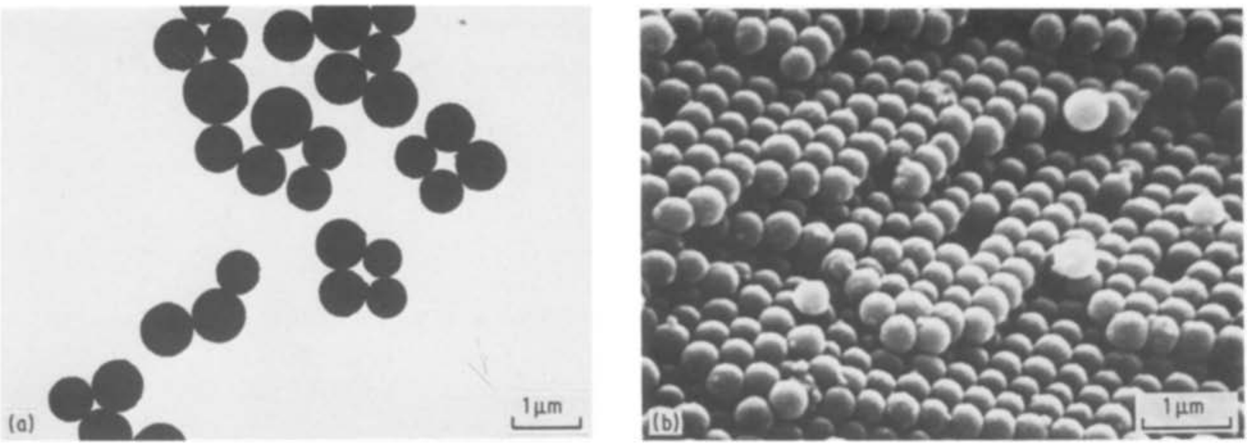

Figure 1 (a) TEM photograph of monodispersed Y-doped ZrO_2 and (b) SEM photograph of the fracture surface of a gravimetrically sedimented compact in a basic suspension. 0.15 mol l^{-1} water, aged for 5 h at 50° C.

TEM (JEOL Ltd, Japan). The crystalline state and size were determined by a powder X-ray diffractometer (Philips, Netherlands). The composition of particles was measured by an energy-dispersive X-ray quantitative analysis, EDX (Nippon Philips Co., Japan) attached to TEM.

3. Results and discussions

Fig. 1a shows a TEM photograph of Y-doped ZrO_2 powder prepared under the conditions of 0.15 mol l^{-1} as a water concentration and at 50° C ageing for 5 h. The particles were spherical, narrow and non-agglomerated with 0.5 μm diameter. Fig. 1b shows an SEM photograph of a fracture surface of the gravimetrically sedimented compact in a basic aqueous solution. The compact contains three dimensional closed packing arrays of particles since they have almost the same sizes and are not agglomerated to each other.

Powder X-ray diffraction and thermal analysis showed that the as-prepared particles were amorphous and hydrated. On heating the water and unreacted alkoxides were released with a weight loss of 20% from 200 to 800° C and the amorphous particles crystallized into a tetragonal single phase around 500° C. However, the morphology of the calcined particles was the same as that of the as-prepared ones. The crystalline size of the particles calcined at 1000° C was calculated according to Hall's equation [13] from the width of the diffraction pattern of the tetragonal (1 1 1) peak to be 55.0 nm.

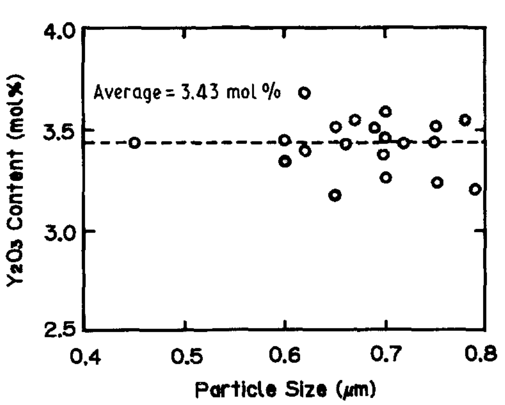

Figure 2 Particle size against Y_2O_3 dopant concentration of each particle by EDX analysis.

Fig. 2 shows the Y_2O_3 dopant level in each particle measured by EDX quantitative analysis. In all the particles determined, Y_2O_3 dopant contents are controlled within the range of 3.4 ± 0.3 mol % and there is independence of particle size.

When the Y-doped ZrO_2 powder was prepared using the co-precipitation of an aqueous solution of Y^{3+} and Zr^{4+}, Zr^{4+} first precipitates and then Y^{3+} does so, with increasing pH on the addition of an aqueous base. As a result, the composition of the precipitated particles does not seem to be constant. Therefore, the high temperature calcination will be required to obtain the homogenization of the composition for all particles [14, 15]. However, it is possible to dope homogeneously in each particle by controlled hydrolysis of alkoxides after fully refluxing $Zr(OC_4H_9)_4$ and $Y(i\text{-}OC_3H_7)_3$ to produce the copolymer of the alkoxide [15]. On the other hand, the particles derived from unrefluxed alkoxide solution are polydispersed and agglomerated. This suggests that each component of the alkoxide solution is heterogeneously mixed and consequently the hydrolysis rates of $Zr(OC_4H_9)_4$ and $Y(i\text{-}OC_3H_7)_3$ are different from each other.

Fig. 3a shows the change of the particle size distribution with the ageing time in ethanol solution. It can be seen that the particle size increased with ageing time but the width of the distribution curve is approximately constant. As a result, the deviations of the particle size become relatively small with particle growth. Fig. 3b shows a TEM photograph of the particles aged for 0.5 h. The 0.5 h aged particles are small and agglomerated and their surface is rough. However, after 5 h ageing the particles (Fig. 1) become larger and spherical and have smooth surfaces. This means that the ageing is necessary to synthesize monodispersed particles.

Water concentration in an alcoholic solution affects particle size, shape, and degree of agglomerate. The precipitation rate is considered to increase with water concentration and affects the morphology of the particles. It is likely that the duration taken for the

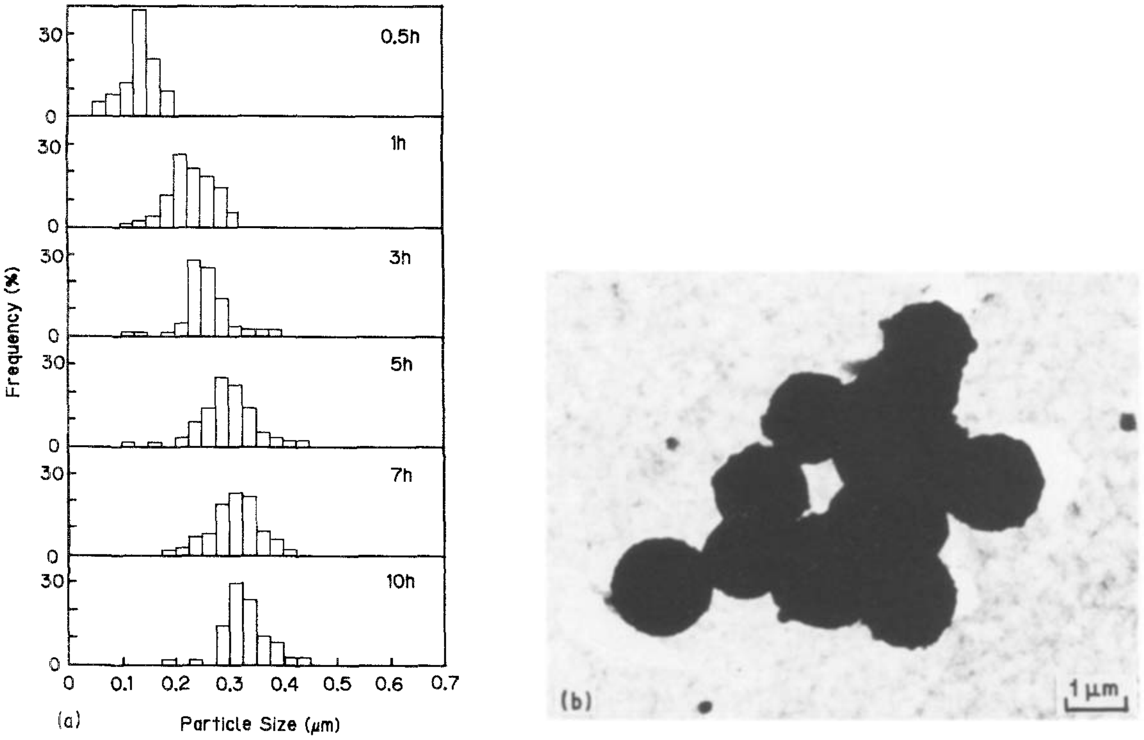

Figure 3 (a) The change of size distribution with ageing time and (b) a TEM photograph of particles aged for 0.5 h. 0.15 mol l^{-1} water, aged at 50° C.

solutions to become turbid is the best criterion for evaluation of the precipitation rate.

Fig. 4a shows the variation of average size, standard deviation and yield of the particle with water concentration under ageing conditions of 3 h at 50° C. It shows that as the water concentration become lower, the particles tend to have a narrower size distribution. However, when the water concentration is less than 0.1 mol l^{-1}, it takes a long time (generally more than 1 h) for precipitation to occur and even if aged for 5 h, the colour of the solution does not change into deep white. This is because the particles are too small and they cannot be separated from the solvent by centrifugation. In lower water concentrations, the precipitation rate is very slow and the particles grow slowly. Hence more ageing is required to grow submicron particles.

In increasing water concentrations, the particles become polydispersed and greatly agglomerated, as shown in Fig. 4b. In this case, the alkoxide solution becomes turbid as soon as water is added. It is considered that the fast precipitation of oxides occurs in this solution and causes the particles to agglomerate.

When the water concentration was 0.15 mol l^{-1}, the particles had the narrowest size distribution. In addition, they were spherical non-agglomerated. Consequently, the best water concentration to make monodispersed particles is about 0.15 mol l^{-1}.

Fig. 5a shows the variation of each parameter, i.e. particle size, yield of particle, standard deviation of particle size, with increasing ageing temperature under the condition of 0.15 mol l^{-1} water for 3 h ageing. The average particle size and yield of particles were increased with increasing ageing temperature, while the best standard deviation is shown to be obtained at 50° C. The particles aged at 30° C are a mixture of

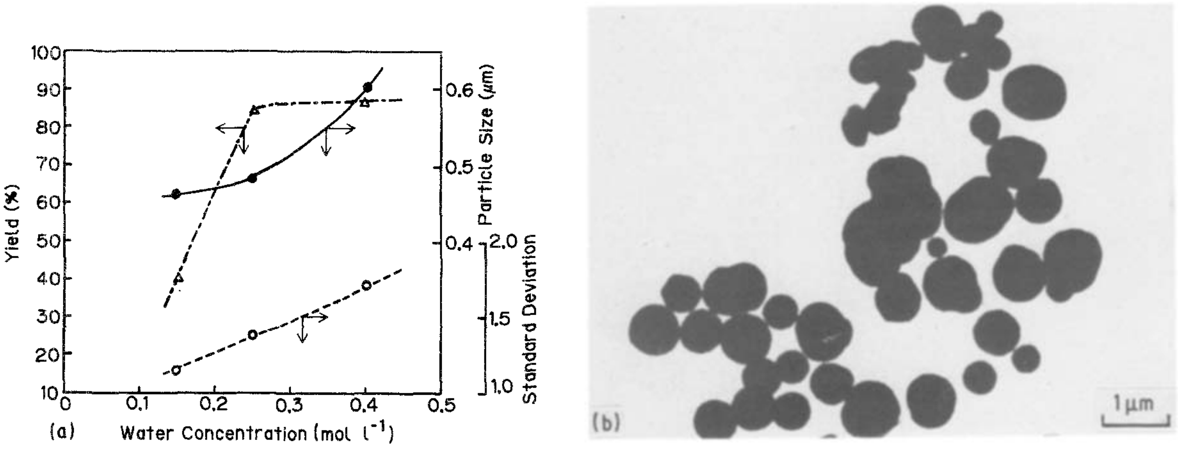

Figure 4 (a) The variations of particle size, standard deviation and yield with water concentration, and (b) a TEM photograph of particles synthesized at 0.40 mol l^{-1} of water. Aged at 50° C for 3 h.

small and larger particles, the smaller particles appearing to stick on the surface of the larger ones, as shown in Fig. 5b.

In the case of 80° C, all particles were very large and were not spherical (Fig. 5c). This phenomenon is due to the fact that generally the higher the temperature leads to the higher the solubility, and the particle size becomes large according to the Weimarn rule [16], i.e. a small number of particles are generated and the rate of hydrolysis is slow because the ratio of Weimarn is small.

In conclusion, Y-doped ZrO_2 ceramic powders prepared by hydrolysis of alkoxide had almost homogeneous Y_2O_3 dopant concentrations within each particle. These powders are considered to be promising as raw materials for TZP and reduce their sintering time and temperature without sintering aids. In the present works, it is possible to adjust the particle size in the range of 0.1 to 1.0 μm by controlling the ageing period. However, the conditions of ageing temperature and water concentration in which monodispersed particles can be obtained are narrowly limited, i.e. 50° C and 0.15 to 0.20 $\text{mol}\,l^{-1}$. To prepare particles larger than 1 μm, the solution must be allowed to age for over 10 h.

We consider the mechanism of particle growth to be as follows: the nucleation of the oxides occurred with the hydrolysis reaction. The particles agglomerated to each other and grew larger during ageing in the alkoxide–ethanol solution. As a result, the polydispersed particles were formed because the rate of assembly of each particle was different. At the same time as this agglomeration, the solute was supplied continuously from the solution and precipitated on the concave surface of the agglomerated particles. If the ageing is done under adequate conditions to synthesize monodispersed particles, the particles grow round and their surfaces become smooth. In addition, the deviation of particle size also becomes smaller with particle growth, as shown in Fig. 3a. Consequently, ageing under adequate conditions is essential for the formation of monodispersed particles.

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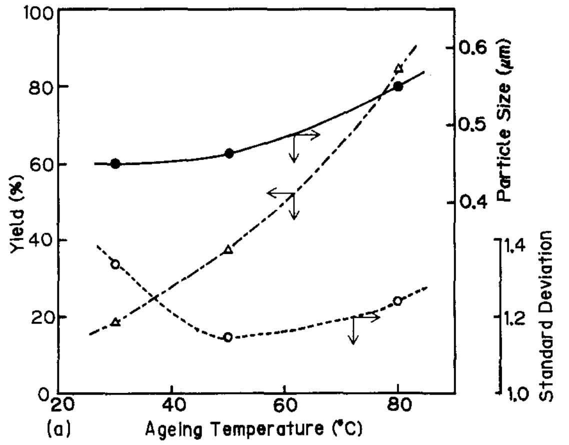
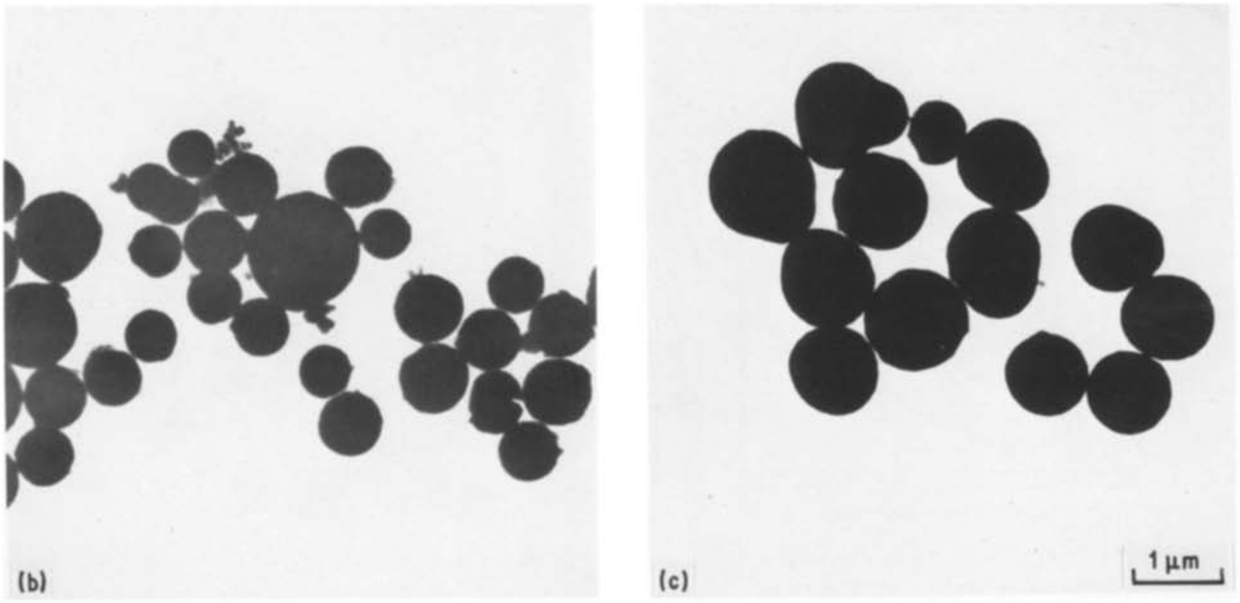


Figure 5 (a) Variations of particle size, standard deviation and yield with ageing temperature and TEM photographs of particles aged at (b) 30° C and (c) 80° C. 0.15 $\text{mol}\,l^{-1}$ water, aged for 3 h.



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