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Crystal growth of tetragonal ZrO_2 in the glass system ZrO_2–SiO_2 prepared by the sol–gel process from metal alkoxides

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Glasses in the system ZrO_2–SiO_2 containing 40 to 60 mol% ZrO_2 were prepared by the sol–gel process from metal alkoxides. Tetragonal ZrO_2 was precipitated by heat treatment at 800 and 1200° C, and its crystal growth was measured by differential thermal and X-ray diffraction analyses. At 800 to 900° C, tetragonal ZrO_2 crystals grew three-dimensionally and the activation energy for growth was calculated as about 680 kJ mol^{-1}. On the other hand, the secondary growth of tetragonal ZrO_2 at 1000 to 1200° C followed the cube-root-of-time law. The activation energy for secondary growth was about 380 kJ mol^{-1}. It is suggested that the diffusion of Zr^{4+} ions is the rate-limiting process for the secondary crystal growth of tetragonal ZrO_2.

1. Introduction

ZrO_2-containing ceramics have recently become of interest because of their high fracture toughness, which has been attributed to the stress-induced transformation of tetragonal ZrO_2 [1–4]. This transformation toughening of ZrO_2 observed in ceramics should be applicable also to an amorphous matrix. In the field of glass technology, ZrO_2 has been used as a nucleating agent [5] to make glass–ceramics in which tetragonal ZrO_2 is observed to precipitate during the crystallization, although its amount is small as a few wt %. Recently, the preparation of ZrO_2 transformation toughening glass–ceramics containing up to 20 to 30 wt % ZrO_2 has been reported [6, 7]. In general, the melting of glasses containing high ZrO_2 is very difficult since it requires a high temperature. On the other hand, using the sol–gel process from metal alkoxides, glasses having high melting temperatures has been obtained at moderate low temperature.

The author has been conducting a study of the preparation of glasses with high ZrO_2 content [8, 9]. Recently, the author and Tomozawa [10] prepared $3ZrO_2 \cdot 2SiO_2$ glass–ceramics in which tetragonal ZrO_2 was precipitated, and then measured their fracture toughness. The fracture toughness increased with increasing size of the tetragonal ZrO_2 crystals. The high fracture toughness of the obtained glass–ceramics was related to the tetragonal-to-monoclinic ZrO_2 transformation.

In the present paper, the crystal growth of tetragonal ZrO_2 in glass–ceramics having various content of ZrO_2 was measured by differential thermal and X-ray diffraction analyses in the temperature range 800 to 1200° C.

2. Experimental procedure

2.1. Sample preparation and crystallization

Three compositions in the system ZrO_2–SiO_2, with 40, 50 and 60 mol % ZrO_2, were studied. $Si(OC_2H_5)_4$ was at first partially hydrolysed by dropping it into a mixed solution of 0.15 mol l^{-1} HCl aqueous solution and C_2H_5OH such that the resulting mixture consists of 1 to 1 mole ratio of H_2O and $Si(OC_2H_5)_4$ and 15 vol % C_2H_5OH. After stirring this solution for 3 h, $Zr(OC_3H_7)_4$ was added drop by drop, followed by stirring for 1 day at room temperature. The solution was poured into a Teflon container and was left with a cover to form a stiff gel. This gel was gradually heated up to 100° C in an atmosphere of 100% relative humidity and then further heated to 150° C and held for 15 h. The gel was then heated at 50° C h^{-1} to about 800° C and kept at that temperature for 1 h, which converted it into non-porous glass. The crystallization heat-treatment of gel and glass was performed at temperatures of up to 1200° C in an air atmosphere.

2.2. Differential thermal analysis

Differential thermal analysis (DTA) was carried out with a Rigaku Denki (Tokyo, Japan) thermal analysis instrument using a sample of about 50 mg powders or particles, a heating rate of 2.5 to 20° C min^{-1}, a static air atmosphere and α-Al_2O_3 as the reference material.

2.3. Powder X-ray diffraction

Tetragonal (t-) ZrO_2 has been observed to transform into monoclinic (m-) ZrO_2 by the stress imposed during crushing into a powder. Therefore, prior to heat treatment, the sample was crushed into powder in order to avoid the stress-induced transformation of t-ZrO_2.

Crystals were characterized by a powder X-ray diffractometer (Rigaku Denki) using nickel-filtered Cu$K\alpha$ radiation. Powder X-ray diffraction (XRD) data were obtained by scanning at a rate of 0.25° (2θ) min^{-1}. The crystallite size of t-ZrO_2 was calculated by Scherrer's formula using the line broadening

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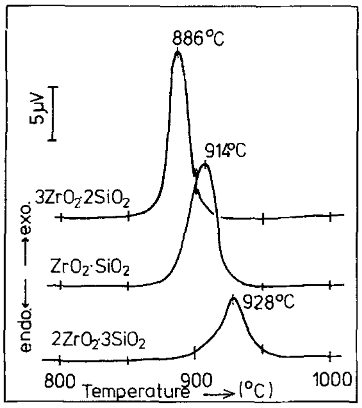

Figure 1 DTA curves for gels of $2ZrO_2 \cdot 3SiO_2$, $ZrO_2 \cdot SiO_2$ and $3ZrO_2 \cdot 2SiO_2$. Heating rate is $10°\,C\,min^{-1}$.

(β) of the (1 0 1) diffraction line. The value of β, defined as the line-width at half peak intensity, was obtained using the Klug–Alexander method [11] from the observed line broadening and the instrumental broadening. The (1 0 1) diffraction line of α-quartz was used as the reference for instrumental broadening. The fraction of $t\text{-}ZrO_2$ precipitated in the glass was calculated by comparing the peak area to that of a pure $t\text{-}ZrO_2$ crystal, which was partially stabilized ZrO_2 prepared by Toray Industries, Inc. (Ohtsu, Japan). The peak area was obtained by weighing a chart paper cut-out of the (1 0 1) line.

3. Results and discussion

3.1. Crystal growth from DTA

The gels are porous and contain physically and chemically adsorbed water on the gel pore surfaces. On heating, the gels liberate the adsorbed water and then transform into impervious, non-porous glasses by the reaction of dehydration–condensation and sintering at the temperature defined as the gel-to-glass conversion temperature, about 800° C, which has been discussed elsewhere [8].

In the DTA trace of gels up to 800° C, only an endothermic peak around 200° C was observed, primarily due to the removal of physically bound water, but no exothermic peak around 300° C due to the carbonization of unhydrolysed metal alkoxides, which indicates that gels prepared by the method of Section 2.1 are completely hydrolysed.

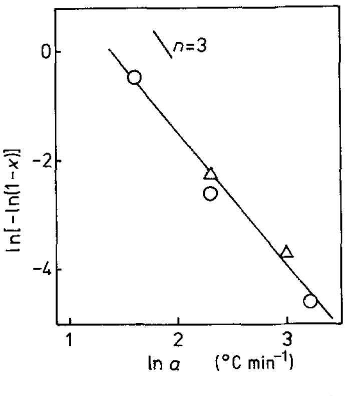

Figure 2 Relation between $\ln[-\ln(1-x)]$ and $\ln a$ for $3ZrO_2 \cdot 2SiO_2$: (○) unheated gel, (△) gel heated at 750° C for 1 h.

The DTA curves above 800° C are shown in Fig. 1, in which the exothermic peak is found at about 900° C. The exothermic peak temperature is a little higher than the gel-to-glass conversion temperature The exothermic peak is seen to lower the peak temperature and increase the intensity with an increase of ZrO_2 content. From the XRD patterns of the samples heated at around peak temperature, this exothermic peak could be attributed to the precipitation of $t\text{-}ZrO_2$. In the peak temperature range, $t\text{-}ZrO_2$ is not stable, but $m\text{-}ZrO_2$ is stable. It has been observed that the metastable $t\text{-}ZrO_2$ initially precipitates in glass–ceramics containing ZrO_2 prepared by the conventional melting process [5–7].

DTA has been used for studying the crystallization kinetics of glass–ceramics by several authors [12–15]. The crystals precipitated in the glass increase their volume and size with increasing temperature, which causes the exothermic peak in the DTA trace.

The volume fraction, x, of crystal precipitating in glass heated at a constant rate, a, was formulated by Matusita *et al.* [15] as follows:

$$\ln[-\ln(1-x)] = -n\ln a - 1.052mE/RT + \text{constant} \qquad (1)$$

where E is the activation energy for crystal growth, R the gas constant, T the temperature and n and m numerical factors depending upon the crystallization mechanism The value of n is equal to m when the nuclei are already formed in the glass before DTA measurement, or $(m+1)$ when the nuclei are formed during the heating for DTA measurement. The volume fraction of crystal which is precipitated up to as certain temperature can be obtained by comparing its peak area to the total peak area under the DTA curve. For the sample of $3ZrO_2 \cdot 2SiO_2$, the volume fraction of crystal precipitated up to 875° C is plotted against the heating rate in Fig. 2. The relation between $\ln[-\ln(1-x)]$ and $\ln a$ gives a straight line with an n value of 2.7. The n value can be taken as 3 because it should be an integer; the value of m may be 2 or 3 depending on the nucleation mechanism. The gel was heated at 750° C for 1 h. This heat treatment was to form the nuclei, if there was no nucleus in the gel. The plot of $\ln[-\ln(1-x)]$ against $\ln a$ for this heat-treated sample is also shown in Fig. 2. It is found that there is no change in the value of n, which indicates that the value of m amounts to 3. This experimental result, that both n and m are 3, suggests that the nuclei

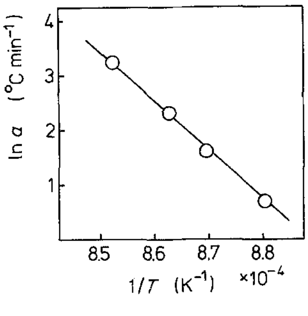

Figure 3 Relation between $\ln a$ and reciprocal peak temperature for $3ZrO_2 \cdot 2SiO_2$.

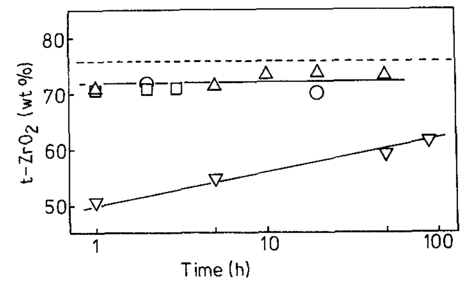

Figure 4 Variation of weight fraction of precipitated t-ZrO$_2$ with heating time for $3ZrO_2 \cdot 2SiO_2$: (▽) 900° C, (○) 1000° C, (△) 1100° C, (□) 1200° C; dotted line = theoretical value.

are formed sufficiently in the gel prepared in this study and the crystal grows three-dimensionally.

According to Equation 1, the plots of ln a against the reciprocal temperature at which the volume fraction of crystal reaches constant give the activation energy for crystal growth. It is known that the volume fraction of crystal at the peak temperature of the DTA curve is the same, about 0.7, irrespective of the heating rate [15]. Fig. 3 shows the relation between ln a and the reciprocal peak temperature. From the slope of the straight line and the m value, the activation energy was calculated as 680 kJ mol^{-1}. The activation energy was also obtained for $2ZrO_2 \cdot 3SiO_2$ and $ZrO_2 \cdot SiO_2$, which gave 660 and 690 kJ mol^{-1}, respectively. The activation energy seems to be independent of the ZrO$_2$ content.

It is generally accepted that the activation energy for crystal growth is equal to that for the viscous flow of glass [16]. The activation energy for viscous flow of glasses prepared in this study has not yet been measured. The activation energy obtained for crystal growth is similar to that for the viscous flow of silica glass, about 670 kJ mol^{-1} [17]. From this and the fact that the nuclei of ZrO$_2$ crystals are formed early in the gel stage, the crystal growth of ZrO$_2$ can be considered to be controlled by the viscous flow of silica surrounding the ZrO$_2$ crystals.

3.2. Secondary growth of t-ZrO$_2$ crystals

In the temperature range of DTA measurement, crystal growth is not very fast. According to this crystal growth, the volume fraction of crystal increases, and reaches a constant value at a higher temperature than the peak temperature of the DTA curve. The fraction of t-ZrO$_2$ calculated by comparing the peak areas of the XRD pattern is shown in Fig. 4 as a function of heating time. The sample is $3ZrO_2 \cdot 2SiO_2$. The dotted line in Fig. 4 is the theoretical ZrO$_2$ content calculated from the composition (75.5 wt %). At 900° C the amount of t-ZrO$_2$ increases with increasing time. At 1000 to 1200° C, on the other hand, the t-ZrO$_2$ content reaches a constant value within a short time, although it is a little smaller than the theoretical one.

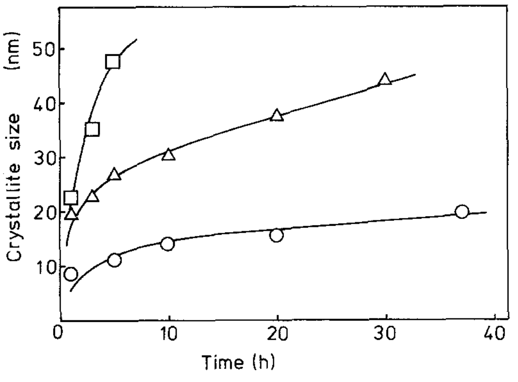

Figure 5 Variation of crystallite size of t-ZrO$_2$ with heating time for $3ZrO_2 \cdot 2SiO_2$: (○) 1000° C, (△) 1100° C, (□) 1200° C.

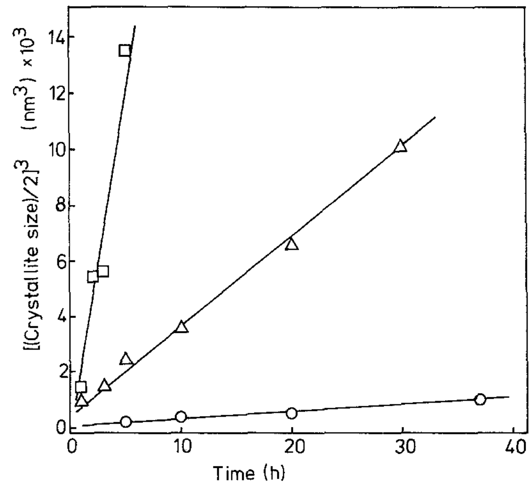

Figure 6 Relation between (crystallite size/2)^3 and heating time for $3ZrO_2 \cdot 2SiO_2$: (○) 1000° C, (△) 1100° C, (□) 1200° C.

In this section, the crystal growth at 1000 to 1200° C is discussed. Fig. 5 shows the change of crystal size (crystallite size) of the t-ZrO$_2$ with heating time. As t-ZrO$_2$ content remained constant during heat treatment, the crystal growth shown in Fig. 5 should be accounted for in terms of diffusion-controlled Ostwald ripening theory, in which smaller particles dissolve and large particles grow by devouring the smaller ones. Ostwald ripening was formulated by Lifshitz and Slyozov [18] and Wagner [19] as follows:

$$\frac{dr}{dt} = \frac{\text{constant}}{r^n}\left(\frac{1}{r_c} - \frac{1}{r}\right) \qquad (2)$$

$$r = \frac{n+1}{n} r_c \qquad (3)$$

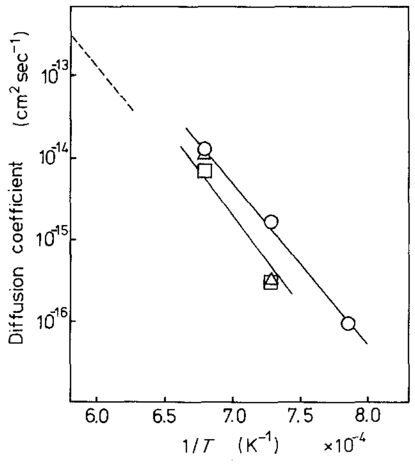

Figure 7 Relation between diffusion coefficient and reciprocal temperature: (□) $2ZrO_2 \cdot 3SiO_2$, (△) $ZrO_2 \cdot SiO_2$, (○) $3ZrO_2 \cdot 2SiO_2$; dotted line = Zr^{4+} ion in ZrO$_2$ [22].

where r is the radius of a particle, t time, r_c the critical radius and n a constant. The constant n is a numerical factor depending on the diffusing process, which is 1 or 2 for bulk diffusion or grain-boundary diffusion, respectively. Integrating Equation 2 for each n value, the time dependence of r is obtained, which is $r^3 = Kt$ (K = constant) or $r^4 = Kt$ for $n = 1$ or 2, respectively. The experimental data of Fig. 5 were found to follow the equation $r^3 = Kt$, as shown in Fig. 6. Therefore, the crystal growth can be attributed to Ostwald ripening by bulk diffusion. According to Wagner's theory [19], the proportionality constant K is given by

$$K = (8\gamma D C_0 V^2)/9RT \qquad (4)$$

where γ is the surface energy, D the diffusion coefficient, C_0 the solubility of particles, V the molar volume, R the gas constant and T the temperature. The diffusion coefficient can be calculated from Equation 4, given appropriate values for γ, C_0 and V. The surface energy, γ, of t-ZrO_2 particles in the glass is not known but here has been taken as $0.7\,J\,m^{-2}$. The value of this surface energy is somewhat controversial, ranging from about 0.6 to $0.8\,J\,m^{-2}$ [20, 21]. The solubility C_0 and the molar volume V are calculated from the composition by assuming that ZrO_2 particles are fully dissociated from the SiO_2 matrix. The diffusion coefficient thus estimated is plotted as a function of reciprocal temperature in Fig. 7, in which the diffusion coefficient of Zr^{4+} ions in ZrO_2 partially stabilized with CaO is also shown as a dotted line [22]. The present data are reasonably consistent with the extrapolated value of diffusion coefficient for ZrO_2. The activation energy obtained is $380\,kJ\,mol^{-1}$ for $3ZrO_2 \cdot 2SiO_2$ and seems to increase a little with decreased ZrO_2 content. These experimental results show that the secondary crystal growth of t-ZrO_2 is controlled by the diffusion of Zr^{4+} ions.

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