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Effect of the size of nuclei on crystallization behavior of $Li_2O \cdot 2SiO_2$ glass

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Crystallization peak temperature was measured for $Li_2O \cdot 2SiO_2$ glass with various number densities of nuclei induced by long heat-treatment (~405 h) at 460°C. Its crystallization process of $Li_2O \cdot 2SiO_2$ glass was simulated numerically in order to examine the effect of the initial size of nuclei on crystallization behavior, and the relationship between crystallization peak temperature and the number density of nuclei in the glass was considered. It was found that the effect of nuclei size is not significant when the heat-treatment temperature is lower than 460°C. By considering the effect of nuclei size, number density of nuclus was evaluated by DTA method accurately.

1. Introduction

Glass ceramics are produced by crystallizing preformed glasses. The process to produce glass ceramics has some advantage compared with the sintering process which is often employed for ceramics production. First, performed glasses can be handled more easily than pressed green compacts. Second, the crystallization of preformed glasses proceeds at lower temperature than sintering process. Then, its production process is simple.

The nucleation process is essential in the production of glass ceramics and nucleation behavior is an important to obtain products with excellent properties and to develop an effective crystallization process. However, the measurement of the number density of nuclei in glasses by microscopic observation is time consuming. A method using DTA was proposed to evaluate the number density of nuclei easily [1, 2]. Though this method was limited to a qualitative evaluation, Ray *et al*. proposed a novel method using DTA, recently [3].

Wakasugi *et al*. have evaluated the number density of nuclei in glass in terms of the crystallization peak temperature, T_C obtained by DTA [4–7]. In the previous paper [7], the relationship between T_C and the number density of nuclei was reported and a calculation of T_C was performed for $Li_2O \cdot 2SiO_2$ glass. It was also shown that, however, the effect of the initial radius of nuclei on crystallization peak temperature should be considered as the number density of nuclei increases or the growth of nuclei becomes significant. In fact, such decrease in T_C was experimentally observed [8].

In this study, the crystallization peak temperature of $Li_2O \cdot 2SiO$ glass heat-treated for long time was measured and the crystallization process was simulated numerically. The effect of the size of nuclei on the crystallization temperature was considered in order to clarify the relationship between T_C and the number density of nuclei in glasses.

2. Experimental

$Li_2O \cdot 2SiO$ glass was prepared from reagent grade of Li_2CO_3 and SiO_2. Well mixed batches were melted in a Pt crucible in an electric furnace at 1300°C for 1 h. The melts were stirred several times to obtain homogeneous glasses and quenched by pressing them between steel plates. The glass was heat treated at 460°C for 144–405 h. Heat-treated glasses were employed for DTA measurement to obtain T_C. DTA measurement (Rigaku TG-8110) was done with a heating rate of 10°C/min using a Pt crucible (5 mmϕ × 5 mm). In order to reduce the effect of surface nucleation, bulk samples were used on DTA run and the surface of samples was removed before DTA measurement to avoid the effect of surface nucleation. To minimize the deviation in the heating rate during crystallizationdue to the heat of crystallization, the weight of sample was adjusted in the range of 10 to 20 mg.

3. Calculation

Followings were assumed before calculation: (1) DTA curve was corresponds to the derivative of volume fraction of crystal with respect to time, (2) nuclei are spherical and grow isotropically on DTA heating, (3) surface nucleation is negligible on DTA measurement. The volume fraction of crystal, α, is expressed as a function of crystal radius, r, by Equation 1 [9], where N is the number density of nuclei.

$$\alpha = 1 - \exp\left(-\frac{4}{3}\pi N r^3\right). \quad (1)$$

When the initial radius of nuclei is neglected, r at a temperature, T, during DTA measurement with a heating rate, Q, is obtained by integrating the crystal growth rate, U, from room temperature, T_0, to T as shown in Equation 2 and U is given by Equation 3 [10].

TABLE I

Parameter	Value	Reference
$\log \eta$/Pa · s	$1.81 + \frac{1350}{T-595} T$: in K)	[11]
ΔH_m	27.0 kJ/molSiO_2	[12]
T_m	1034°C	[12]
c	0.209 m · Pa^{-1}	[6]

$$r = \frac{1}{Q}\int_{T_0}^{T} U \, dT + r_{ini}, \tag{2}$$

$$U = \frac{c}{\eta}\left[1 - \exp\left(\frac{\Delta H_m (T - T_m)}{RTT_m}\right)\right], \tag{3}$$

where r_{ini} is the radius of nuclei before DTA measurement, and η, R, ΔH_m and T_m are viscosity, gas constant, enthalpy change at melting and melting temperature, respectively. "c" is a constant determined from experiment. The DTA curve responds to $d\alpha/dt$ as shown in Equation 4. The values of these parameters for $Li_2O \cdot 2SiO_2$ glass are shown in Table I.

$$\frac{d\alpha}{dT} = \frac{4\pi N}{Q} r^2 U (1-\alpha) \tag{4}$$

T_C is the temperature where $d\alpha/dT$ becomes maximum. Then, the temperature where $d^2\alpha/dT^2$ shown in Equation 5 becomes zero was calculated and determined as T_C.

$$\left(\frac{d^2\alpha}{dT^2}\right) = \frac{4\pi N}{Q}\left[2r\frac{dr}{dt}\cdot\frac{dt}{dT}U(1-\alpha) + r^2\frac{dU}{dT}(1-\alpha) - r^2 U\frac{4\pi N}{Q}r^2 U(1-\alpha)\right]$$
$$= \frac{4\pi N}{Q} r(1-\alpha) \times \left[\frac{2U^2}{Q} + \frac{dU}{dT}r - \frac{4\pi N}{Q}U^2 r^3\right] \tag{5}$$

The relationship between the obtained T_C and the number density of nuclei, N, is expressed in Fig. 1. In this figure, T_C was calculated assuming that $r_{ini} = 0$. However, the growth of nuclei during the isothermal heat-treatment should be considered as the heat-treatment time increases.

In the previous paper [7], it was shown that the growth of nuclei during the nucleation heat-treatment lowers the T_C as the number density of nuclei increases. And a little disagreement in T_C between experiments and calculation was also shown. This agreement would be explained in terms of the size effect of nuclei, and this effect is considered, here. Assuming that the induction time for steady state nucleation is very short or negligible, the number of nuclei increases linearly with heat-treating time, t. When the number density after the nucleation heat-treatment for t_0 is N, the average nucleation rate is N/t_0. The radius of the nuclei which were formed during isothermal heating at

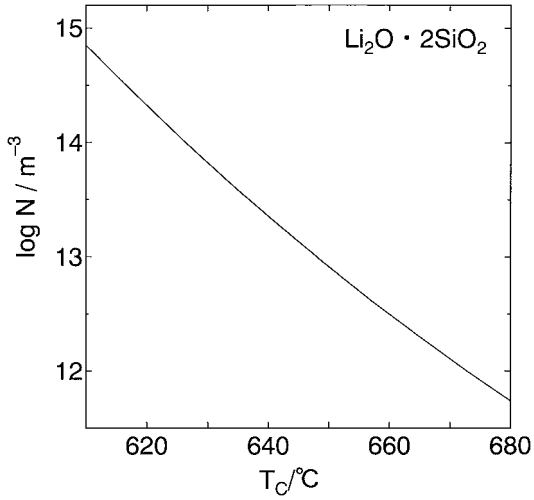

Figure 1 Calculated relationship between the number density of nuclei, N, and T_C.

time, t, and grown on DTA heating from T_0 to T, is $U_{NT}(t_0 - t) + r'$, where, U_{NT} is the crystal growth rate at nucleation temperature and r' is the growth of nuclei during DTA measurement, $\frac{1}{Q}\int_{T_0}^{T} U \, dT$. The increase of volume fraction contributed by these nuclei is $4\pi(U_{NT}(t_0 - t) + r)^2 \, dr(1-\alpha)\frac{N}{t_0} dt$. The total increase of the volume fraction of crystal, $d\alpha$, is expressed as Equation 6, where $r_0 = U_{NT} t_0$ is the radius of the nuclei formed at the beginning of the heat-treatment.

$$d\alpha = \int_0^{t_0} 4\pi \frac{N}{t_0}(U_{NT}(t_0 - t) + r')^2 \, dt(1-\alpha)\, dr$$
$$= 4\pi N(1-\alpha)\left(r'^2 + r_0 r' + \frac{1}{3}r_0^2\right) dr. \tag{6}$$

It should be noticed that $dr = dr'$. Then, α is obtained as Equation 7 instead of Equation 1.

$$\alpha = 1 - \exp\left[-\frac{2\pi N}{3}\left(2r'^3 + 3r_0 r'^2 + 2r_0^2 r'\right)\right]. \tag{7}$$

Equation 7 becomes same as Equation 1 when $r_0 = 0$. The second order derivative of α shown in Equation 7 with respect to T is expressed as follows, where $U = Q \cdot dr'/dT$.

$$\frac{d^2\alpha}{dT^2} = \frac{2\pi N}{3Q}(1-\alpha)\left[-\frac{2\pi N}{3Q}U^2\left(6r'^2 + 6r_0 r' + 2r_0^2\right)^2 + \frac{dU}{dT}\left(6r'^2 + 6r_0 r' + 2r_0^2\right) + \frac{U^2}{Q}(12r' + 6r_0)\right] \tag{8}$$

The calculation of T_C based of this equation was also performed.

4. Results and discussion

The variation of T_C for $Li_2O \cdot 2SiO_2$ glass heat-treated at 460°C with heat-treatment time, t_0, is shown in Fig. 2 together with the data in the previous report [7]. The standard deviation in T_C was 1.5°C when DTA measurement was performed four times for the samples

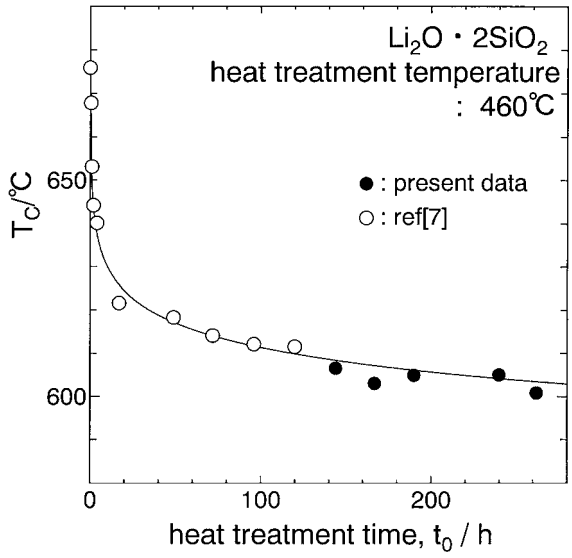

Figure 2 Variation of T_C for $Li_2O \cdot 2SiO$ glass heat-treated at 460°C with heat-treatment time. The line is a guide for eyes.

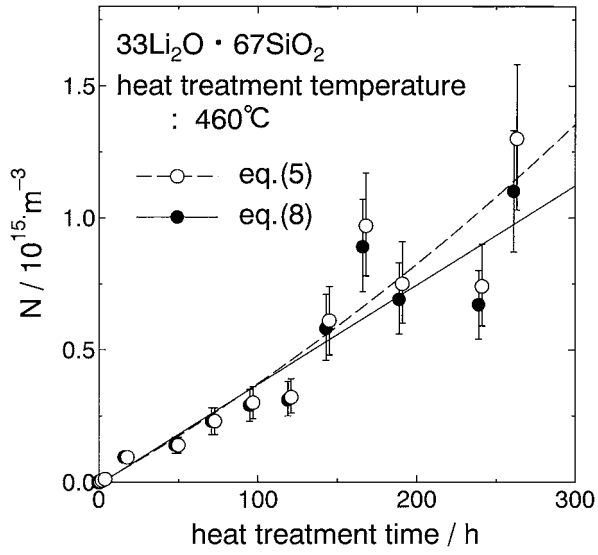

Figure 3 Variation of the number density of nuclei, N, for $Li_2O \cdot 2SiO$ glass heat-treated at 460°C with heat-treatment time calculated by using Equations 5 and 8. Lines are guides for eyes.

heat-treated under the same condition (460°C, 17 h). T_C decreased with heat-treatment time monotonically and this decrease corresponds to the increase of the number density of nuclei. Then it was found that the nucleation proceeds for 262 h without saturation. The number density of nuclei was estimated from the T_C by using Equation 5 and shown in Fig. 3 by open circles. The error bar in Fig. 3 corresponds to the standard deviation for T_C.

Since it is reported that $Li_2O \cdot 2SiO_2$ glass shows steady state nucleation within 1 or 2 hours at 460°C [11], a linear relationship between nucleation time and the number density of nuclei should be obtained. However, the slope of the line in Fig. 3 seems to increase with the increase of the heat-treatment time. This apparent increase of nucleation rate would have been caused by some reasons: the effect of size of nuclei on T_C, or an error in the evaluation of crystal growth rate. Among them, the effect of size of nuclei (size effect) will be considered in the following.

In Equation 5, the size of nuclei before DTA measurement was neglected. It was reported that the XRD pattern for $33.3Li_2O \cdot 66.7SiO_2$ glass heat-treated at 454°C for 328 h showed weak peaks of the stable $Li_2O \cdot 2SiO_2$ phase emerged [13]. Other investigators also reported that the precipitation of crystalline phase after log heat-treatment around [14–16]. These facts means the $Li_2O \cdot 2SiO_2$ glass crystallizes partially even at 460°C where crystal growth rate is very low, when heat-treatment time is very long. The evaluation of size effect becomes important under these conditions.

Since T_C decreases with the increase of not only the number density of nuclei but also the size of nuclei [7], the number density of nuclei in the sample with long heat-treatment tends to be overestimated. This might cause the apparent increase of nucleation rate. Then, the number density of nuclei was re-evaluated with Equation 8 and it was also shown in Fig. 3 by solid circles. It was found that the size effect becomes large as the heat-treatment time increases and the linearity of the line seems to be good. However, the difference in T_C by considering the size effect is not clear compared with the error in N. From the slope obtained by a linear regression of these data, the nucleation rate was calculated to be $1.0 \times 10^9/m^3 \cdot s$ at 460°C which roughly agrees with the reported value [11, 17–20].

Of course, the heat treatment time necessary for the effect of the growth of nuclei to become remarkable depends on the heat-treatment temperature. Fig. 4 shows the difference between T_C calculated with Equations 5 and 8, ΔT_C. The calculation was performed for the heat-treatment temperatures of 460, 480, and 500°C. The nucleation rate was evaluated from the literatures [11, 17–19]; 2.82×10^9, 0.96×10^9 and $0.16 \times 10^9/m^3 \cdot s$ at 460, 480 and 500°C, respectively. T_C obtained by Equation 5 was always higher than that by Equation 8. The result at 440°C was not shown in this figure because ΔT_C was less than 0.1°C even for 400 h. ΔT_C becomes large at 480 and 500°C and the effect of nuclei growth cannot be neglected. On the other hand, it is found that the size of nuclei can be treated as zero at the temperature lower than 460°C. This fact is very important to evaluate the number density from T_C accurately because Equation 8 was derived with the

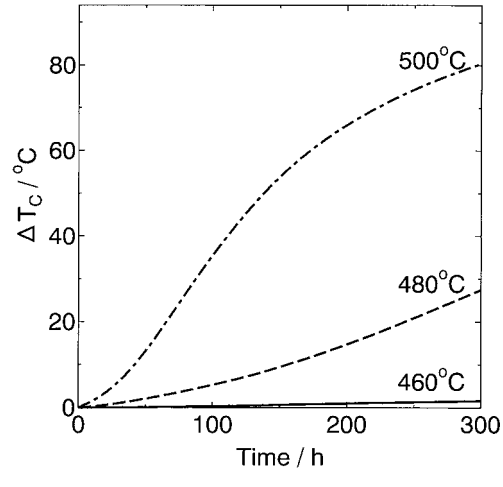

Figure 4 Effect of the growth of nuclei on T_C for $Li_2O \cdot 2SiO$ glass. ΔT_C is the difference between T_C calculated according to Equations 5 and 8.

assumption of no induction time for nucleation. At the temperature range where the induction time is not negligible, the effect of the growth of nuclei is so small that it is not necessary to consider this effect. This relationship would be applicable to other glasses of which their induction time is not known.

The decrease of T_C by the growth of nuclei gives an advantage in the estimation of the number density from T_C. The variation of T_C becomes insensitive to the change of the number density of nuclei as the number density increases if the growth of nuclei does not proceed. The decrease of T_C by the growth of nuclei becomes significant at this insensitive region, so that the accuracy in the evaluation of the number density of nuclei from T_C increases.

5. Conclusions

(1) From the calculation of crystallization process, T_C was obtained as a function of temperature in considering of the size of nuclei.

(2) The crystallization peak temperature of $Li_2O \cdot 2SiO_2$ glasses heat treated at 460°C was measured by DTA in order to evaluate the number density of nuclei and it was confirmed that the nucleation proceeds for 262 h.

(3) The nucleation rate obtained in this study was in agreement with literatures, which means the validity of the evaluation of the number density from T_C.

(4) The effect of the growth of nuclei on T_C for $Li_2O \cdot 2SiO_2$ glass is not significant at 460°C, but should be considered at higher than 460°C.

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