Strength of Li₂O–SiO₂-System Transparent Glass-Ceramics

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Li₂O–SiO₂ 系透明結晶化ガラスの強度

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The relationship between fracture strength and crystal size in the Li₂O–SiO₂-system transparent glass-ceramics was investigated. The precipitated crystal phase, percent crystallinity and crystal size were Li₂O·2SiO₂, 60–80% and 20–60 nm, respectively, following heat treatment below 800°C for 5–144 h. It is found that fracture strength increases linearly with increasing crystal size in the range of 20–60 nm for both non abraded and abraded specimens. Fracture strength can be expressed as a function of crystal size, d (nm), by

$$\sigma = 100.5 + 2.32d \text{ (MPa) [Non-abraded]}$$

$$\sigma = 56.3 + 0.99d \text{ (MPa) [Abraded]}$$

This result shows the opposite tendency for previous result of glass-ceramics of micrometer order crystals. This indicates that very fine crystals cannot effectively interrupt crack propagation, and hence, the stress required for changing the direction of propagation might be small. It can be considered that a critical crystal size may exist for the attainment of the maximum strength. [Received November 17, 2003; Accepted February 5, 2004]

Key-words : Li₂O–SiO₂ system, Transparent glass-ceramics, Nanocrystals, Fracture strength

1. Introduction

One of the significant characteristics of glass-ceramics is that they are stronger than that of glass. Although glass is a typical brittle material that readily fractures, its theoretical strength is quite high (≈ 10 GPa). However, the practical strength of glass is below 50–100 Mpa. Griffith¹⁾ introduced the “Griffith flaw theory” to explain this phenomena. On the reason is that various kind of flaw existing on the surface act as stress concentrator. A higher strength close to the theoretical strength could be obtained by thin fiber or by removing surface flaws.

Generally, the high strength of glass-ceramics represents practical strength. It is recognized that crystals dispersed in glass-ceramics prevent flaw generation or crack propagation.

Many studies on the relationship between fracture strength and crystal size have carried out for glass-ceramics^{2),3)} and sintered polycrystalline materials.^{4),5)} It is confirmed that fracture strength increases with decreasing crystal size on the basis of Griffith's equation assuming that the crystal size is equal to the crack size in a micrometer-order crystal [$\sigma \propto d^{-1/2}$].⁶⁾ According to this idea, the fracture strength of very fine grained sintered polycrystalline materials and glass-ceramics, e.g., transparent glass-ceramics, should be very high. However, the fracture strength of very fine grained transparent glass-ceramics is not so different from that of conventional glass, hence, this idea is not applicable to these materials.

We investigated the relationship between the fracture strength and crystal size of Li₂O–SiO₂-system transparent glass-ceramics and found that fracture strength increases with increasing crystal size up to 100 nm.

2. Experiment

2.1 Sample preparation

The composition of the glass used is 80SiO₂·4Al₂O₃·

13Li₂O·3P₂O₅ (mass%) [77.7SiO₂·2.3Al₂O₃·18.8Li₂O·1.2P₂O₅ (mol%)]. High-purity silica sand, alumina and reagent grade chemicals of Li₂CO₃ and (NH₄)₂HPO₄ (Carlo Erba) were used as raw materials. A batch corresponding to 200 g of glass was mixed thoroughly and precalcined at 400°C overnight to remove NH₃. Then it was melted in a 100 ml Pt/Rh10 crucible at 1450°C for 3 h in an electric furnace.

A rod about 5 mm diameter was freshly drawn and cut into about 7 cm long sample for strength measurement. The samples were then annealed at 450°C for 30 min and cooled to room temperature in the furnace. They were then heat-treated for crystallization under various conditions.

The densities of glass and glass-ceramics were measured by the He-gas substitution method using Accupyc 1330 (Micromeritics).

2.2 DTA, XRD, SEM

A differential thermal analysis (DTA) was carried out routinely to determine the crystallization temperature at a heating rate of 10 K/min using a Perkin-Elmer DTA-7.

Crystalline phases were examined by powder X-ray diffraction analysis (XRD) (Bruker, AXS Model D5005). Crystalline size was calculated using Scherrer's equation.

$$d = 0.9 \cdot \lambda / \beta \cdot \cos \theta \quad (1)$$

Where d is the crystalline size (Å), λ the wavelength of X-ray (1.54 Å), β the true half width (radian) and θ the diffraction angle (degree). True half width was determined by the Jones method,⁷⁾ and α -quartz was used as a standard.

Percent crystallinity was determined using Ohlberg and Strickler's method,⁸⁾ and was calculated using by:

$$\text{Percent crystallinity (\%C)} = 100x(I_g - I_x) / (I_g - I_c), \quad (2)$$

where I_g is the background intensity of glass, I_x that of the

specimens and I_c that of the crystal at $2\theta = 23^\circ$. The calibration curve was obtained using mixtures α -quartz and a parent glass at various ratios, and showed a good linearity.

The surface structures of the nonabraded and abraded specimens were observed by scanning electron micrograph (SEM) (JEOL JSM 6400).

2.3 Strength measurement

The fracture strengths of annealed glass and glass-ceramics were measured using Instron Model 5569 according to ASTM C-158. The three-point bending method was employed and the surface of the specimens was abraded with #180 SiC abrasive paper before the measurement, and the strength of the non-abraded specimens was also measured. The span length and loading rate were 50 mm and 10 mm/min, respectively.

3. Results

3.1 Properties of glass-ceramics

Figure 1 shows the DTA run. Two exothermic peaks appeared at around 600°C and 800°C; the former peak corresponds to the precipitation of the Li₂O·2SiO₂ crystal and latter corresponds to the α -quartz. Figure 2 shows the XRD patterns of glass-ceramics. The main crystalline phase is Li₂O·2SiO₂ at a lower temperature and for a shorter time of crystallization. However, a considerable amount of α -quartz crystal precipitates at a higher temperature for longer time, particularly above 800°C. The percent crystallinity and crystal size ranged from 60 to 75% and from 20 to 60 nm, respectively, below 800°C. The transparent glass-ceramics can be obtained by heat-treatment below 800°C. The density of glass-ceramics increases with increasing heating temperature and time of crystallization.

Table 1 summarizes the heat-treatment conditions, appearance, density, precipitated crystalline phases, percent crystallinity, crystal size, non-abraded and abraded fracture strength of glass-ceramics.

3.2 Effect of percent crystallinity on strength

Figure 3 shows the relationship between fracture strength and percent crystallinity. Both the non-abraded and abraded fracture strength increase with increasing percent crystallinity up to 75–80%. However, the strength does not depend on the percent crystallinity at this region; it depends on another factor, namely, crystal size.

3.3 Effect of crystal size on strength

Figure 4 shows the relationship between fracture strength and crystal size of the non-abraded and abraded specimens. Figure 5 shows the surface structure of non-abraded and abraded specimens. The non-abraded specimens have a very smooth surface, while scratches of various types and sizes in all directions can be observed on the surface of the abraded specimen.

Although the fracture strength is slightly low for the sample with lower percent crystallinity, it is found that fracture strength increases linearly with increasing crystal size for both

Fig. 1. DTA run. Heating rate: 10 k/min.

Fig. 2. XRD patterns of some glass-ceramics. First heat treatment: 500°C-15 h.

non-abraded and abraded specimens, and it can be expressed by the following equation as a function of crystal size, d (nm). The fracture strength of the abraded specimens is about one half that of the non-abraded specimens.

$$\sigma = 100.5 + 2.32d \text{ (MPa) [Non-abraded]}$$

$$\sigma = 56.3 + 0.99d \text{ (MPa) [Abraded]}$$

These calculations were carried out without glass and glass-ceramics of low percent crystallinity.

4. Discussion

As observed above, the abraded and non-abraded fracture strength of the Li₂O-SiO₂-system transparent glass-ceramics increases with increasing crystal size ranging from 20 to 60 nm.

There are many factors affecting the strength of glass and glass-ceramics, and they may be classified into internal structure and surface structure.⁹⁾ The factors resulting from the internal structure are void (pore), difference in thermal expansion coefficient, percent crystallinity and crystal size. In glass-ceramics, the influence of void and the difference in thermal expansion coefficient may be disregarded, and also, the effect of surface structure can also be disregarded. Therefore, only the influences of percent crystallinity and crystal size should be regarded as affecting fracture strength.

Concerning the fracture strength of polycrystalline materials and glass-ceramics, two mechanisms have been proposed. One is the intergranular fracture in which the crack propagates along with the grain boundary and another is the transgranular fracture in which the crack propagates in the grain. The

Table 1. Properties of Glass and Transparent Glass-Ceramics

2nd heat treatment (°C-Hr)* ¹⁾	Appearance	Density (g/cm ³)	Crystalline Phases (XRD)	Percent Crystallinity (±5%)	Crystal Size (nm)	Fracture strength (MPa)* ²⁾
Glass	Transparent	2.3541	—	—	—	122.8±21.7 56.8±6.4
600-96	Transparent	2.3810	Li ₂ O·2SiO ₂	59	22.6	— 68.7±6.7
-144	Transparent	2.3907	Li ₂ O·2SiO ₂	60	24.3	— 67.7±5.6
650-48	Transparent	2.3880	Li ₂ O·2SiO ₂	67	24.2	— 78.5±5.7
-75	Slightly translucent	2.4096	Li ₂ O·2SiO ₂	66	27.1	151.8±36.2 78.3±6
700-24	Slightly translucent	2.4161	Li ₂ O·2SiO ₂	72	28.0	187.9±41.3 82.7±10.5
-48	Slightly translucent	2.4114	Li ₂ O·2SiO ₂	74	31.2	161.7±29.8 90.6±6.5
750-15	Slightly translucent	2.4213	Li ₂ O·2SiO ₂ Li ₂ O·SiO ₂ (very slight)	75	34.0	176.9±49.7 90.6±9.8
-24	Slightly translucent	2.4385	Li ₂ O·2SiO ₂ Li ₂ O·SiO ₂ (very slight)	72	35.8	179.1±30.3 96.5±6.5
775-5	Weakly translucent	2.4385	Li ₂ O·2SiO ₂ , Li ₂ O·SiO ₂ (very slight) α-Quartz(very slight)	77	42.1	205.6±14.4 98.9±9.4
-15	Weakly translucent	2.4358	Li ₂ O·2SiO ₂ , Li ₂ O·SiO ₂ (very slight) α-Quartz(slight)	77	60.2	238.8±49.6 113.3±12.8
800-5	Translucent	2.5053	Li ₂ O·2SiO ₂ α-Quartz	—	—	—

*1): 1st heat treatment:500°C-15 hr. *2): upper: non-abraded, lower: abraded.

Fig. 3. Effect of percent crystallinity on the fracture strength.

Fig. 4. Effect of crystal size on non-abraded and abraded fracture strength.

Fig. 5. SEM images of the surface of non-abraded and abraded specimens. (a) Non-abraded specimen, (b) Abraded specimen.

higher strength of glass-ceramics can be explained by the term of interruption of crack propagation by crystal grain. When the crack propagates along with the grain boundary in polycrystalline or glass-ceramic materials, crack front runs into crystals, which changes the direction of crack propagation. In this case, a higher stress is required to maintain crack propagation. For example, as the crack propagation direction changes by 60° , a stress of 1.8 times higher than that of normal direction may be required, and 4 times larger stress is required for 90° . This is the reason glass-ceramics exhibits higher strengths. In this situation, the crystal size can be accounted for by Griffith's crack size, and thus, fracture strength is proportional to the reciprocal of crystal size ($\sigma \propto d^{-1/n}$). Many experimental results²⁾⁻⁵⁾ confirmed this relation for sintered polycrystalline materials and glass-ceramics of micrometer-order of crystal size; however, the n term differs among researchers. This equation clearly indicates that fracture strength increases with decreasing crystal size.

By assuming the limitation of $d \rightarrow 0$ (glass), the fracture strength must reach the theoretical strength according to the

above theory. However, as is well known, the practical fracture strength of glass is quite low compared to the theoretical strength. The present result also indicates that fracture strength increases with increasing crystal size of nanometer-order of crystals. This implies that the above principle is not applicable to a very fine grained glass-ceramics.

The present result shows that very fine crystals cannot effectively interrupt the crack propagation. Because a crack propagates along with the grain boundary, the change in direction of crack propagation may be much smaller than that for larger grain, and hence, the stress required for the change in direction may be small. Consequently, the fracture strength of very fine grained glass-ceramics is estimated to be small. It should also be noted that a critical crystal size may exist for attaining the maximum fracture strength of polycrystalline and glass-ceramic materials based on above results.

5. Conclusion

The relationship between fracture strength and crystal size of the Li_2O - SiO_2 -system transparent glass-ceramics was investigated and the following results were obtained.

- (1) The precipitated crystal phase, percent crystallinity and crystal size were $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$, 60–80% and 20–60 nm, respectively, following heat-treatment below 800°C for 5–144 h.
- (2) Fracture strength increases linearly with increasing crystal size ranging from 20–60 nm. This can be expressed by

$$\sigma = 100.5 + 2.32d \text{ (MPa) [Non-abraded]}$$

$$\sigma = 56.3 + 0.99d \text{ (MPa) [Abraded]}$$

- (3) Very fine crystals cannot effectively interrupt crack propagation. Therefore, the stress required for changing the direction of propagation may be small.

- (4) It can be considered that a critical crystal size may exist for the attainment of maximum strength.

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