Strengthening of Li$_2$O·2SiO$_2$ Transparent Glass-Ceramics by Ion Exchange

Chokchai YATONGCHAI and Shigeki MORIMOTO

イオン交換法による Li$_2$O·2SiO$_2$ 系透明結晶化ガラスの強化

Chokchai Yatongchai・森本繁樹

School of Ceramic Engineering, Institute of Engineering, Suranaree University of Technology,
111 University Avenue, Muang District Nakhon Ratchasima 30000, Thailand

The chemical strengthening of Li$_2$O·2SiO$_2$ transparent glass-ceramics was investigated. The fracture strength of glass and glass-ceramics increased first and then decreased, and the crack formation and peeling of ion exchanged layer were observed for both Li$^+$↔Na$^+$ and Li$^+$↔K$^+$ ion exchange. This suggests that the submicroscopic crack generates perpendicular to the surface when the ion exchanged layer peels off from the surface. The volume change by Li$^+$↔Na$^+$ and Li$^+$↔K$^+$ ion exchange is very large, over 10%, this large volume change causes the peeing and crack formation of ion exchanged layer despite in which the compressive stress arise. In the early stage of ion exchange, the compressive stress arisen affects effectively on the increase in strength. However, as increase in the thickness of ion exchanged layer, the volume change of ion exchanged layer can not be neglected, and crack and peeling may generate in that layer. Finally, the fracture strength decreases.

1. Introduction

Transparent glass-ceramics comprises the essential group in glass-ceramics, is composed of fine-grained crystallites, usually nano-scale size, and residual glassy phase. The transparent glass-ceramics has been developed and used for many applications, such as transparent cookware, precision optical instruments, ring-laser gyroscope, large telescope mirror blanks, etc. Further, recently, active ions, transition metal ion and rare-earth ion, doped transparent glass-ceramics are developed and many researches on this materials have been carried out.[1]–[4]

Li$_2$O–SiO$_2$ system of glass has well been known as a base glass for glass-ceramics, such as chemically machinable glass-ceramics and high strength glass-ceramics. And also, transparent glass-ceramics based on lithium metasilicate[Li$_2$O·SiO$_2$] and lithium disilicate[Li$_2$O·2SiO$_2$] crystals can be obtained easily in this system of glass.[5],[6] However, the mechanical strength of transparent glass-ceramics is not so high,[7] similar to that of glass, and hence the higher mechanical strength is required in special application area.

There are two methods to increase mechanical strength of glasses and glass-ceramics, thermal strengthening and chemical strengthening. The latter is called as ion exchange strengthening method and has many advantages over thermal strengthening, such as easy processing, available for any shapes of articles, available for thin articles, available to maintain the surface flatness and smoothness, capable of applying for low thermal expansion materials, etc. Li$^+$–Na$^+$ and Li$^+$–K$^+$ ion exchange is expected to increase mechanical strength of these transparent glass-ceramics.

Here the chemical strengthening of Li$_2$O·2SiO$_2$ transparent glass-ceramics was investigated.

2. Experiments

2.1 Sample preparation

The composition of glass used is 80SiO$_2$·4Al$_2$O$_3$·13Li$_2$O·3P$_2$O$_5$ (mass%) [72.9SiO$_2$·2.15Al$_2$O$_3$·23.8Li$_2$O·1.15P$_2$O$_5$ (mol%)]. High purity silica sand, alumina and reagent grade chemicals of Li$_2$CO$_3$ and (NH$_4$)$_2$HPO$_4$ (Aldrich) were used as raw materials. A batch corresponding to 200 g of glass was mixed thoroughly and pre-calcined at 300°C for overnight to remove NH$_3$. Then it was melted in a 100 ml Pt/Rh10 crucible at 1450°C for 2 h in an electric furnace. The molten glass was poured onto iron plate and crushed, and then it was melted at the same condition to improve homogeneity.

A rod about 5 mm diameter was freshly drawn and cut into about 7 cm long. The samples were annealed at 450°C for 30 min and cooled to room temperature in the furnace.

The samples were heat treated at 500°C for 15 h for nucleation and 700°C for 10 h for crystallization.

2.2 Ion exchange

The samples were ion exchanged in NaNO$_3$ and KNO$_3$ molten bath under various conditions (Salt/glass ratio is 10 by weight).

2.3 XRD and SEM

Crystalline phases and lattice constant were determined by powder X-ray diffraction analysis (XRD) (Bruker, AXS Model D5005). Si powder was used as an internal standard for the measurement of the lattice constant. The surface structure of glasses and glass-ceramics after ion exchange were observed by scanning electron microscopy (SEM; JEOL, JSM 640).

2.4 Strength measurement

The fracture strength was measured using Instron Model 5569 according to ASTM C–158. The three point bending method was employed, and the span length and loading rate were 50 mm and 1 mm/min, respectively.

3. Results and discussion

The glass transition temperature (T_g), dilatometric softening point (Y_p), thermal expansion coefficient (α) and density of glass were 473°C, 541°C, 88.9×10^{-7}/K (30–300°C) and 2.354 g/cm^3, respectively. The main crystal, percent crystallinity and crystallite size of glass-ceramics were Li$_2$O·2SiO$_2$ crystal (JCPDS 40–0376), about 70% and 40 nm, respectively. The thermal expansion coefficient and density of transparent glass-ceramics were 90×10^{-7}/K (30–300°C) and 2.414 g/cm^3.

Table 1. Fracture Strength of Glass and Glass-Ceramics before and after Ion Exchange

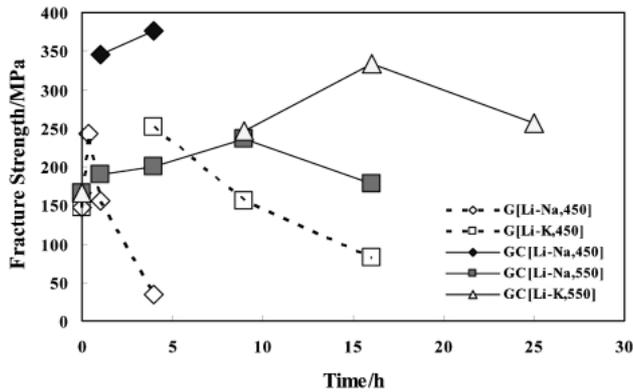| Ion exchange condition (°C–h)	Fracture strength/MPa and appearance*	
	$Li^-\leftrightarrow Na^-$	$Li^+\leftrightarrow K^+$
Glass –	146.4	146.4
450-0.4	243	–
450-1	156	–
450-4	34.7(crack)	250.9
450-9	–	154.9
450-16	–	82(crack)
Glass-Ceramics –	166.5	166.5
450-1	345	–
450-4	376.3	–
450-16	–	288
550-1	189(peeling)	–
550-4	200(peeling)	–
550-9	236(peeling)	246
550-16	178(peeling)	333
550-25	–	256

*: determined by naked eye

Fig. 1. Fracture strength of glass and glass-ceramics before and after ion exchange.

Table 1 shows the fracture strength and appearance of glass and glass-ceramics before and after ion exchange, $Li^+\leftrightarrow Na^+$ and $Li^+\leftrightarrow K^+$. **Figure 1** shows the relation between fracture strength and ion exchange time.

In the case of glass, the fracture strength increases first and then decreases markedly, and a crack generation was observed by naked eye with progress of ion exchange for $Li^+\leftrightarrow Na^+$ and $Li^+\leftrightarrow K^+$ exchange. The rate of ion exchange for $Li^+\leftrightarrow Na^+$ is greater than that for $Li^+\leftrightarrow K^+$ exchange.

The change in fracture strength of glass-ceramics with time shows the similar tendency to that of glass. However, the rate of ion exchange is much slower compared with that of glass. The fracture strength of glass-ceramics increases significantly for both the $Li^+\leftrightarrow Na^+$ and $Li^+\leftrightarrow K^+$ exchange at 450°C. At higher temperature (550°C), the fracture strength increases at first and then decreases gradually. The peeling off of ion exchanged layer was observed for $Li^+\leftrightarrow Na^+$ exchange by naked eye.

Figure 2 shows the SEM photos of the surface of glass and glass-ceramics after ion exchange. It is interesting to note that
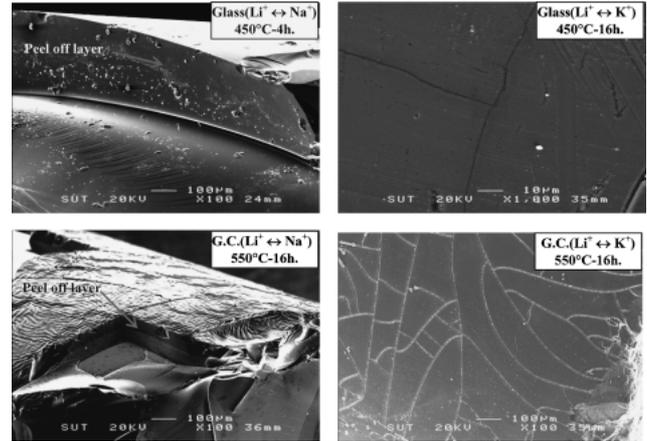
Fig. 2. SEM photos of glass and glass-ceramics after ion exchange.

Table 2. Calculated Density, Molar Volume and Thermal Expansion Coefficient of Li-, Na- and K-Glasses[10]

Glass	Density(g/cm³)	Molar volume (cm³/mol)	ΔV*/% (Li^+–M^+)	α(x10^{-7}/K)
Li-glass	2.36	23.20	–	89.5
Na-glass	2.41	25.88	11.6	119.1
K-glass	2.48	28.22	21.6	135.7

*: change in molar volume after ion exchange(calculated value)

the ion exchanged layer of glass and glass-ceramics peels off from the surface by $Li^+\leftrightarrow Na^+$ exchange. The surface of glass is smooth, but that of glass-ceramics appears to be wrinkling. A hair-like crack can be observed on the surface just below the peeled off layer for glass and glass-ceramics. On the contrary for $Li^+\leftrightarrow K^+$ exchange, cracks can be observed on the surface of glass-ceramics and some irregular spots and cracks emerge for glass. Thus the surface of glass and glass-ceramics shows the abnormal behavior after ion exchange. The relation between this abnormal behavior of surface and the strength will be discussed below.

Generally, it is well known that the brittle materials like glasses are weak in tensile stress, and the ion exchange strengthening can be achieved due to the compressive stress arisen in the surface layer by the replacement of smaller ions in glass by larger foreign ions. This method is called "Crowding".[8] The maximum compressive stress arisen by this mechanism may be given:

$$\sigma_c = (1/3) \cdot [E/(1-\mu)] \cdot (\Delta V/V) \qquad (1)$$

where V is the volume of glass, ΔV the volume change by ion exchange without stress at room temperatue, E the Young's modulus and μ the Poisson's ratio. This equation indicates that the larger ΔV gives the larger compressive stress.

Table 2 shows the calculated density, molar volume and thermal expansion coefficient of Li-, Na- and K-glasses.[9] Assuming that $E = 70$ GPa, $\mu = 0.2$, $\Delta V/V = 2.78/23.10 = 0.12$, then $\sigma_c = 3.5$ GPa for $Li^+\leftrightarrow Na^+$ exchange.[10] And $\Delta V/V = 0.22$ and $\sigma_c = 6.5$ GPa for $Li^+\leftrightarrow K^+$ exchange. The volume change of glass-ceramics is much larger than that of glass by ion exchange because of higher density of glass-ceramics.

It should be noted here that $Li_2O \cdot 2SiO_2$ crystal in the ion exchanged layer of glass-ceramics was destroyed and disap-

peared with progress of ion exchange (This phenomena will be discussed elsewhere). However, the volume and thermal expansion coefficient of this glassy phase is much larger than those of glass-ceramics, and therefore the same treatment as glass might be possible.

The calculated volume change of this glass, $\Delta V/V$, is very large, however, this value must be much smaller actually, and hence the compressive stress arisen is estimated to be much lower, 800–1000 MPa. It is very interesting to note that the peeling and crack formation occur despite a large compressive stress arise in ion exchanged layer. The peeling and crack formation are not observed in a usual ion exchange process. In the early stage of ion exchange discussed here, peeling and crack formation were not observed for glass and glass-ceramics, therefore, the compressive stress arisen affects effectively on the increase in strength. However, as increase in the thickness of ion exchanged layer, the volume change of ion exchanged layer can not be neglected, and crack and peeling may generate in that layer. It is considered that this large volume change anyhow causes the peeling and crack formation of ion exchange layer. With progress of ion exchange, the peeling and crack formation take place and the submicroscopic crack (hair-like crack in Fig. 2), which acts as stress concentrator, generates perpendicular to the surface and finally the fracture strength decreases.

The volume change of ion exchanged layer strongly depends on the alkali content in the base glass. The glass discussed here contains about 24 mol% of Li_2O. These peeling and crack formation seems to be the characteristics of high alkali containing glasses by ion exchange.

4. Conclusion

The chemical strengthening of $Li_2O \cdot 2SiO_2$ transparent glass-ceramics was investigated. The fracture strength of glass and glass-ceramics increased first and then decreased, and the crack formation and peeling of ion exchanged layer were observed for both $Li^+ \leftrightarrow Na^+$ and $Li^+ \leftrightarrow K^+$ ion exchange. This suggests that the submicroscopic crack generates perpendicular to the surface when the ion exchanged layer peels off from the surface.

The calculated volume change by $Li^+ \leftrightarrow Na^+$ and $Li^+ \leftrightarrow K^+$ ion exchange is very large, over 10%, this large volume change causes the peeing and crack formation of ion exchanged layer despite in which the large compressive stress arise. In the early stage of ion exchange, the compressive stress arisen affects effectively on the increase in strength. However, as increase in the thickness of ion exchanged layer, the volume change of ion exchanged layer can not be neglected, and crack and peeling may generate in that layer. Finally, the fracture strength decreases.

References

1) Morimoto, S., *J. Ceram. Soc. Japan*, Vol. 112, pp. 486–490 (2004).
2) Wu, X., Yuan, H., Yen, W. M. and Aitken, B. G., *J. Luminescence*, Vol. 66&67, pp. 285–289 (1996).
3) Downey, K. E., et al., Proc. Cleo 2001, CuP1, Vol. 1, pp. 211–212, Chiba, Japan (2001).
4) Jewell, J. M., Friebe, E. J. and Aggarwal, I. D., *J. Non-Cryst. Solids*, Vol. 188, pp. 285–288 (1995).
5) McMillan, P. W., "Glass-Ceramics," Academic Press, London (1979).
6) Morimoto, S., *J. Luminescence*, submitted.
7) Morimoto, S. and Emem, W., *J. Ceram. Soc. Japan*, Vol. 112, pp. 259–262 (2004).
8) Kistler, S. S., *J. Am. Ceram. Soc.*, Vol. 45, pp. 59–64 (1962).
9) Volf, M. B., "Mathematical Approach to Glass," Elsevier, Amsterdam (1988).
10) Beall, G. H., Karstetter, B. R. and Rittler, H. L., *J. Am. Ceram. Soc.*, Vol. 45, pp. 181–186 (1967).