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Improvement of chemical durability of high expansion glasses by ion exchange

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In order to prepare a high expansion glass with good chemical durability, $Na_2O \cdot 2SiO_2$ glass was ion-exchanged in molten $LiNO_3$ at 460 to 520° C. A Li_2O rich layer, of 100 to 200 μm thickness, was produced on the glass surface. Corrosion rate in hot water (98° C) and thermal expansion coefficient were measured. The thin layer on the surface had a much lower corrosion rate in hot water and a lower expansion coefficient than the bulk glass. Because the ion-exchanged layer was thin with respect to the bulk glass, an overall high expansion was maintained. However, it acted as a protective layer giving rise to improved chemical durability.

1. Introduction

Inorganic glasses laminated to plastics form window systems of great importance because of safety considerations. Thermal expansion coefficients of glasses, however, are usually very low compared with those of plastics. For example, typical window glass has an expansion coefficient of about 90×10^{-7} °C^{-1} [1], and polystyrene about 600×10^{-7} °C^{-1} [2]. Even the very low expansion plastic, polyphenylene oxide, has an expansion coefficient of 270×10^{-7} °C^{-1} [3]. Stress would develop at the glass–plastic interface when the temperature is changed leading to delamination or fracture. The stress, σ, can be estimated from

$$\sigma = (T_1 - T_2)(\alpha_P - \alpha_G)\frac{E_P E_G}{E_P + E_G}$$

where T_1 is the temperature of lamination, T_2 is the temperature of use, α_P and α_G are the thermal expansion coefficients of plastic and glass, and E_P and E_G are Young's moduli of plastic and glass. When the window glass ($E_G = 10 \times 10^6$ p.s.i.) [1] is laminated to polystyrene ($E_P = 5 \times 10^5$ p.s.i.) [2] at 150° C, assuming no stress relaxation occurs, then the resultant stress at 20° C is about 3000 p.s.i., and even when window glass is laminated to polyphenylene oxide ($E_P = 4 \times 10^5$ p.s.i.) [3], the stress would be about 1000 p.s.i. These stresses are significant when compared to the tensile strength of glass (10 000 p.s.i.) [1] and plastics (3000 to 10 000 p.s.i.) [2]. Inorganic glasses of high expansion coefficients are obviously desirable. For example, if a glass of expansion coefficient of 160×10^{-7} °C^{-1} is laminated to polyphenylene oxide, the stress would be 600 p.s.i., almost half of the 1000 p.s.i. for a soda-lime window glass laminate.

In general, however, inorganic glasses of high expansion usually have poor chemical durability [4–6]. This is exemplified by the behaviour of high expansion phosphate glasses [6]. If the concentration of alkali oxide is increased, the expansion coefficient is increased while the chemical durability is decreased. For the different alkali oxides, expansion coefficient increases and chemical durability decreases with increasing cationic size. One possible way of preparing glasses with high expansion coefficients and good chemical durability is by forming a thin durable layer on the surface of a high expansion glass. Thermal expansion is determined by the bulk of the sample and chemical durability is controlled by the thin surface layer. Three methods to make a thin layer are possible:

(1) Ion exchange of high expansion glasses in

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molten salt to form a thin chemically durable layer on the surface.

(2) Dealkalization of the surfaces of high expansion glasses to form an alkali-free layer. Usually alkali-free silicate glasses have good durability [5].

(3) Bonding of a thin durable glass to the surface of a high expansion glass.

If these layers are made at high temperatures, surface compressive stresses would develop on cooling if the expansion coefficient of the surface layer is less than that of the underlying bulk glass. This is feasible since chemically durable glasses usually have low expansion coefficients. Therefore, these methods can also be used to increase the strength of high expansion glasses [7–10].

This report is concerned with the preparation of high expansion glasses which have good chemical durability, by the method of ion exchange. It is well known that Na_2O-SiO_2 glasses have high expansion coefficients and poor chemical durability as compared to Li_2O-SiO_2 glasses [4, 5]. A glass of composition $Na_2O \cdot 2SiO_2$ was selected as the high expansion glass and treated in molten $LiNO_3$ just above the glass transition temperature to form a thin Li_2O-rich layer on the surface. The thermal expansion coefficient and the corrosion rate in hot water were measured. It was found that a high expansion glass with good chemical durability could indeed be prepared by the ion-exchange process.

2. Experimental procedures

The $Na_2O \cdot 2SiO_2$ glass was prepared from reagent grade silicic acid and sodium carbonate. About 80 g was placed in a platinum crucible and melted in an electric furnace at 1400° C for 24 h. The melt was then poured into graphite moulds. Chemical analysis showed that the glass contained 33.7 mol% Na_2O and 66.3 mol% SiO_2. The glass was stored in kerosene. Prior to ion exchange, the samples were washed with benzene and dried. The sample was first heated at 300° C for 20 min and then immersed in molten $LiNO_3$ in a stainless steel vessel. The ion-exchange temperature was controlled to within ± 2° C by an Omega Engineering Controller Model 49.

As a measure of chemical durability, the weight loss in 98° C water was measured by using plate-shaped samples with a surface area 10 to 15 cm^2. The volume of water was always kept at 500 ml during the measurement. The corrosion rate, K, was determined by,

$$K = \Delta W/St \qquad (1)$$

where ΔW is weight loss (g) in time t (min), and S is the surface area (cm^2) of the solid specimen. The immersion time was within 160 min. Thermal expansion coefficients were measured with a Leitz Universal Dilatometer Model UBD. Tensile strengths of abraded samples before and after ion exchange were measured with an Instron Testing Machine Model TM-S. In order to measure the thickness of the chemically durable layer, the ion-exchanged glass (Fig. 1a) was fractured (Fig. 1b) and the fracture surface was immersed in boiling water for 5 min (Fig. 1c). The bulk glass was partially dissolved and the ion-exchanged layer remained, as shown in Fig. 1d. The thickness of the layer was then measured under a microscope. Fig. 2 shows the example of such a durable layer.

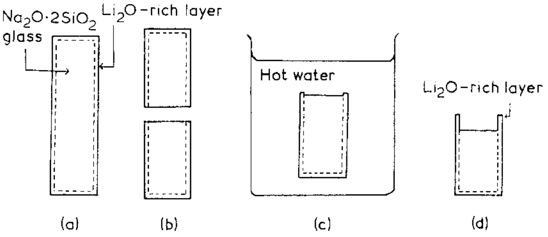

Figure 1 Method of measurement of thickness of durable layer. (a) Ion-exchanged glass; (b) fracture of ion-exchanged glass; (c) immersion of the fractured glass in hot water; (d) thickness of Li_2O-rich layer revealed.

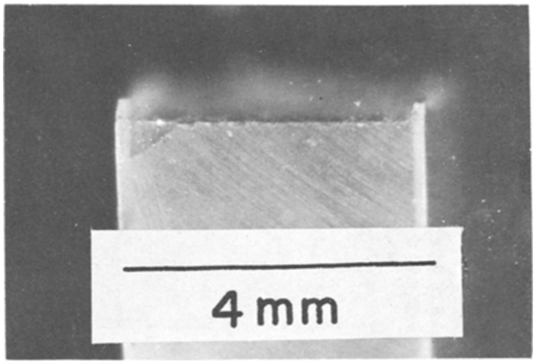

Figure 2 Durable layer produced by ion exchange at 480° C for 5 min, and treated by the method shown in Fig. 1.

3. Experimental results

The thickness of the durable layer produced by ion exchange in $LiNO_3$ is shown in Fig. 3 as a function of ion-exchange temperature. Fig. 4 shows the variation of the thickness of the durable layer with ion-exchange time in $LiNO_3$ at 480° C. The thickness is seen to increase with the square root of time, indicating that the ion exchange is controlled by diffusion. Fig. 5 shows the weight loss of the sample immersed in hot water (98° C) as a function of time. Weight loss is seen to increase linearly with time. The dissolution rates obtained from the slopes of such plots are shown in Table I, together with expansion coefficients. The strengths of the sample before and after ion exchange (480° C, 5 min) are shown in Table I. The glass transition temperature of the original glass was 440° C.

TABLE I Corrosion rate in water at 98° C, thermal expansion coefficient and tensile strength of $Na_2O \cdot 2SiO_2$ glass before and after ion exchange (molten salt; $LiNO_3$, ion-exchange time; 5 min).

Ion-exchange temperature (° C)	K (g cm^{-2} min^{-1})	$\alpha \times 10^7$ (deg^{-1})	σ (p.s.i.)
$Li_2O \cdot 2SiO_2$	5.3×10^{-6}	120	
Original glass	5.0×10^{-3}	168	11 600 ± 2700
460	1.1×10^{-5}		
480	9.0×10^{-6}	155	14 500 ± 1600
500	1.2×10^{-5}		
520	9.2×10^{-6}	154	

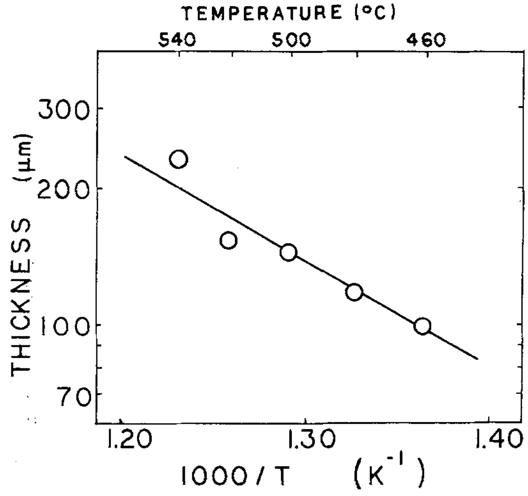

Figure 3 Thickness of durable layer versus reciprocal of ion-exchange temperature. Ion-exchange time: 5 min.

4. Discussion

Ion-exchange strengthening of glasses has been studied by many workers [10–12]. If the Li^+ ions from the salt replace the Na^+ ions in the glass at a temperature below T_g, the resultant glass surface will be in tension since the radius of the Li^+ ion (0.65 Å) is less than that of the Na^+ ion (0.95 Å) [8]. If such exchange occurs just above T_g, stress relaxation can occur although the material is practically solid and no tensile stress will be formed on the surface [5]. On the other hand, because the ion-exchange time need only be short as 5 min, no distortion of the sample was observable even though the exchange took place just above T_g. In the present study, Na^+ ions in the glass were replaced by Li^+ ions just above T_g. The thickness of the durable layer which is Li_2O-rich increased linearly with the square root of time, as shown in Fig. 4. This seems to indicate that the ion exchange was controlled by diffusion.

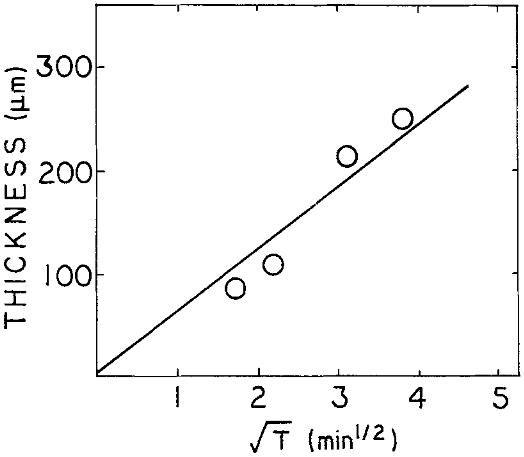

Figure 4 Thickness of durable layer versus ion-exchange time. Ion-exchange temperature: 480° C.

The activation energy for the apparent interdiffusion calculated from the slope of Fig. 3 is 12 kcal mol^{-1}. The activation energies for Li^+ diffusion in Na_2O-SiO_2 and that for Na^+ in Li_2O-SiO_2 glasses at temperatures just above T_g are not known. The activation energy for diffusion of Na^+ ions in $Na_2O \cdot 2SiO_2$ glass is reported to be about 16 kcal mol^{-1} near T_g, and for Li^+ in $Li_2O \cdot 2SiO_2$ glass at below T_g it is also about 16 kcal mol^{-1} [13–15]. The physical meaning of the lower activation energy of the present study is thus difficult to explain.

The durable layer on the surface is Li_2O-rich. The thermal expansion coefficient of $Li_2O \cdot 2SiO_2$ glass is lower than that of $Na_2O \cdot 2SiO_2$ glass as shown in Table I. Therefore, compressive stresses are expected to develop during cooling. Fig. 6

shows the bright surface compression layer observed under an optical microscope. The apparent increase in strength by the ion-exchange process is shown in Table I. The thermal expansion coefficient of the ion-exchanged glass is only slightly lower than that of the original glass. The slight decrease in expansion coefficient is probably due to the existence of the low expansion surface layer. This phenomenon was also observed by Stookey *et al.* for $Na_2O-Al_2O_3-SiO_2$ glasses [8]. Fig. 7 shows the electron microprobe NaKα profile of the glass ion-exchanged at 460° C for 5 min. Only a small amount of Na^+ ion is seen to remain on the surface. It is difficult to determine the amount of Na^+ ion quantitatively by electron microprobe analysis, but it is apparent that most of the Na^+ ions at the surface were replaced by the Li^+ ions from the molten salt. As a result, the corrosion rate in hot water decreased by some three orders of magnitude after ion exchange, as shown in Fig. 5. The corrosion rate is fairly uniform for all ion-exchange temperatures, as shown in Table I. This indicates that the surface chemical composition is similar for all ion-exchange temperatures. The present study indicates that it is thus feasible to prepare other high expansion glasses and to improve their chemical durability similarly by the proper choice of a bulk glass and the appropriate molten salts.

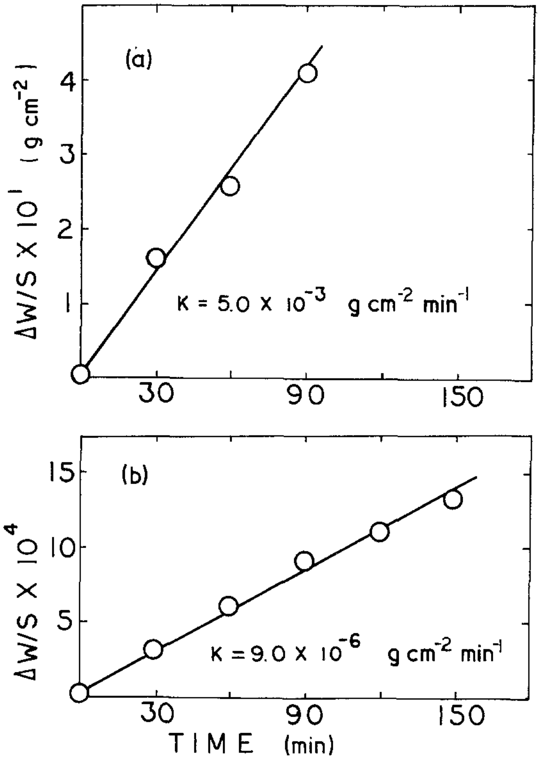

Figure 5 Weight loss per unit surface area of sample in hot water (98° C). (a) Before ion exchange; (b) After ion exchange at 480° C for 5 min.

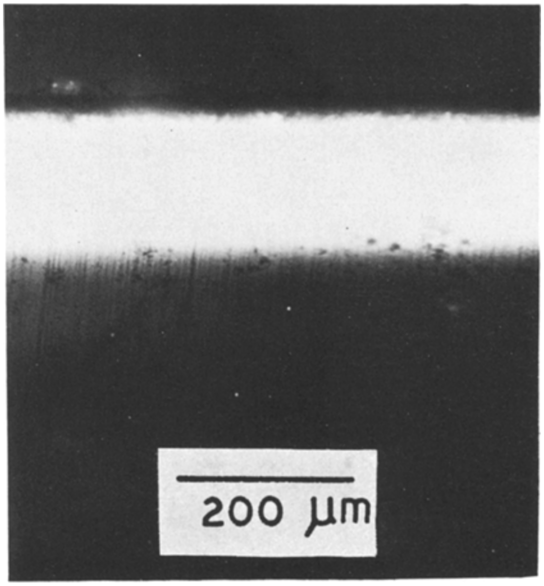

Figure 6 Surface compression layer after ion exchange as seen under polarized light.

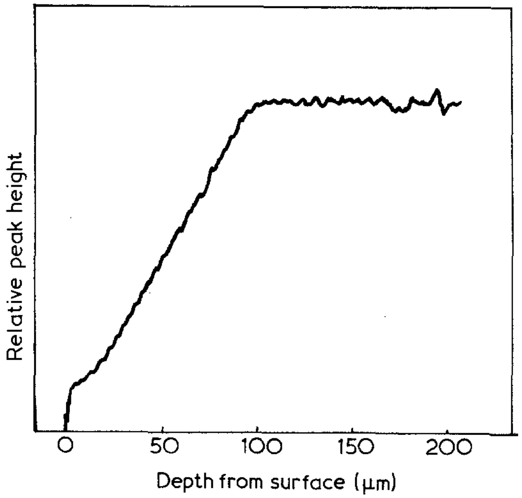

Figure 7 Electron microprobe profile of NaKα in the glass ion exchanged at 480° C for 5 min.

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