Improvement of chemical durability of high expansion phosphate glass by ion-exchange

Window systems of inorganic glasses laminated to plastics are important because of safety considerations. Thermal expansion coefficients of glasses, however, are very low compared with those of plastics, and when the temperature is changed, the stress would develop at the glass–plastic interface leading to undesirable phenomena, such as delamination or fracture. Inorganic glasses of high thermal expansion coefficients are thus desired. In general, however, inorganic glasses of high expansion coefficients usually have poor chemical durability [1–3]. One possible way to prepare glasses of high expansion and good chemical durability is by forming a thin durable layer on the surface of a high expansion glass [4]. In the previous paper, the authors found that ion-exchange above the glass transition temperature was a good method to form such a layer on high expansion glass, while maintaining a high expansion coefficient [4]. Also surface compressive stresses were developed on cooling because the thermal expansion coefficient of the surface layer was less than that of the underlying bulk glass, which was then strengthened [4–6].

In the present study, the chemical durability of potassium aluminophosphate glass was improved by ion-exchange in NaCl–$ZnCl_2$ molten salt mixtures. Although the ion-exchange of silicate glasses have been studied extensively [6], no study has been reported on the ion-exchange between phosphate glasses and molten salts.

The glass composition chosen in this study was $33K_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ (mole ratio). This glass was reported to have a much higher expansion coefficient and poorer chemical durability than $33Na_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ glass [3]. The batch was placed in a platinum crucible and melted at 1000° C for 2 h in an electric furnace. The melt was poured in to a stainless steel mould and annealed. The glass was stored in kerosene. Prior to ion-exchange, the samples were washed with benzene and dried in air. The sample was heated at 280° C for 20 min and then immersed in molten salt. The ion-exchange temperature was 400° C and controlled to within ± 2° C by an Omega Engineering Controller Model 49. The molten salt used for the ion-exchange was NaCl–$ZnCl_2$ mixture (mole ratio 1:1) because this binary system had a low liquidus temperature [7]. Thermal expansion coefficient and corrosion rate in hot water were measured as described in the previous paper [4]. The glass transition temperature of the original glass determined from thermal expansion curves was 290° C. Table I shows the thermal expansion coefficient of the glasses between 25 and 250° C and the corrosion rate in 98° C water before and after ion-exchange. The thermal expansion coefficient of the ion-exchanged glass is

TABLE I Thermal expansion coefficient and corrosion rate in 98° C water

	$\alpha \times 10^7$ (° C^{-1})	K (g cm^{-2} min^{-1})
$33K_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ (before ion-exchange)	220	3.1×10^{-4}
Ion-exchange at 400° C for 20 min	205	7.6×10^{-6}
$33Na_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$	138	6.2×10^{-6}

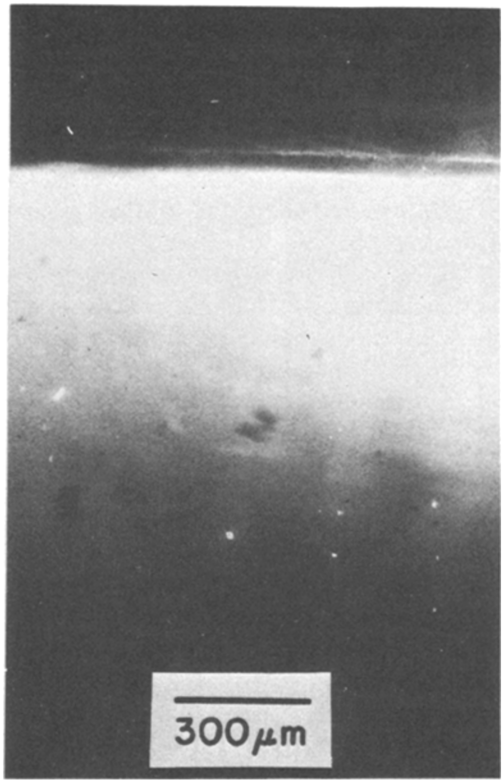

Figure 1 Compressive stress layer developed by the ion-exchange at 400° C for 20 min.

slightly lower than that of the original glass. This decrease in the expansion coefficient is probably due to the existence of a low expansion surface layer. This phenomenon has been observed already [4–5]. The corrosion rate decreased to almost the same value of $33Na_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ glass, indicating that most of the K^+ ions on the glass surface were replaced by Na^+ ions from the molten salt. Since the $33Na_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ glass has lower expansion coefficient than $33K_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ glass as shown in Table I, compressive stresses were expected to develop on the surface after cooling. Fig. 1 indeed shows the bright surface layer observed under a polarized optical microscope, indicative of the compression developed on the glass surface.

It can be concluded that the chemical durability of $33K_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ glass was improved to almost the same value of $33Na_2O \cdot 7Al_2O_3 \cdot 60P_2O_5$ glass while maintaining a high thermal expansion coefficient. The glass obtained in the present study has much higher expansion coefficient and slightly better chemical durability than that obtained in the previous study in which the $Na_2O \cdot 2SiO_2$ glass was ion-exchanged in $LiNO_3$ salt ($\alpha = 155 \times 10^{-7}\,{}^\circ C^{-1}$, $K = 1.0 \times 10^{-5}\,g\,cm^{-2}\,min^{-1}$) [4]. By the proper choice of a bulk glass and the appropriate molten salts, it is possible to prepare other glasses of high expansion and good chemical durability by this method.

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Chemical etchants to reveal old and fresh dislocations in MgO crystals

Most of the dislocation etchants of {1 0 0} faces of MgO crystals reported in the literature [1–3] form shallower and often smaller etch pits at old dislocations. Because of the behaviour of the etchants, it is likely that several dislocations are either not revealed at all or go unobserved because of the shallowness and small size of etch pits. Consequently, the use of the reported etchants may lead to an erroneous picture of the dislocation density and distribution in MgO crystals. In this letter are reported several solutions of aliphatic acids that reveal fresh and old dislocations on {1 0 0} faces of MgO crystals.

For experimental purposes we employed polished {1 0 0} MgO surfaces. Initially formic, acetic and propionic acids of different concentrations were tried in the temperature interval 25 to 80° C. Formic acid below 7 N formed shallow etch pits at old dislocations, while above 7 N produced pyramidal elevations and therefore was found unsuitable. Acetic and propionic acids at low concentrations yielded a rough surface with shallow etch pits or pyramidal elevations similar to those formed by formic acid. At concentrations above 8.7 and 6.6 N, acetic and propionic acids respectively, formed deep and contrastive etch pits, at sub-boundaries and in grains. These pits were of an equal size, more or less, to that of pits produced at slip bands (Figs.