JOURNAL OF MATERIALS SCIENCE 23 (1988) 2797–2809

Preparation and mechanical behaviour of some chemically strengthened lithium magnesium alumino-silicate glasses

I. W. DONALD, M. J. C. HILL
Atomic Weapons Establishment, Aldermaston, Berkshire, UK

Chemically strengthened lithium magnesium alumino-silicate glasses have been prepared by ion-exchange in sodium nitrate at 385° C, and the stress profiles of the resultant materials have been measured using the scattered light and etching technique. Unusual stress profiles have been obtained for some of the materials, with the outermost layers of the surface being in tension, rather than compression. This effect can be eliminated, however, by addition of Na_2O to the glass batch; after ion-exchange treatment, these materials exhibit the normal, relaxed stress profiles associated with many chemically strengthened glasses. The mechanical properties of the materials, both with and without Na_2O additions, have also been measured using a biaxial flexure method. The strongest glass exhibits a high strength, in the as-treated condition, of $\sim$860 MPa.

1. Introduction

Because fracture is almost invariably initiated from the surface of brittle solids, it is feasible to increase the strength of such materials by placing the surface in compression. One method by which this can be achieved is to cool the glass rapidly from a temperature above the glass transition temperature, T_g. Rapid cooling, in this sense, involves quenching by air jets or, more recently, by jets of liquid or even gas fluidized particulate matter [1], directed at the glass surface. This process gives rise to the familiar "toughened", or "tempered" glass. The surface compression, together with a balancing internal tensile stress, arises due to differences in quenching rate, and hence "solidification" rate, between the glass interior and the glass surface. The magnitude of the surface compressive stresses attainable by thermal routes is, however, limited by a number of factors, including the maximum practical cooling rate that can be achieved, the thermal expansion characteristics of the glass, and geometrical considerations, all of which generally limit the method for use with glass articles of relatively simple shape, and thicknesses greater than about 2 mm. The maximum strength realized in practice is of the order of 350 MPa, which is approximately four to five times stronger than that of the untreated glass. The theory and practice of thermal strengthening has been reviewed in detail recently by Gardon [2].

In addition to thermal treatments to yield compressive surface stresses, chemical methods are also feasible. Chemical methods have the distinct advantage that almost any geometry can be used and, in addition, very thin sections < 2 mm thick can be employed, because the method does not rely on the setting up of thermal gradients. Furthermore, unlike thermal strengthening, glasses with low thermal expansion coefficients can be treated successfully by ion-exchange methods. Treatment is also carried out at a temperature $< T_g$ so that problems associated with viscous deformation and subsequent distortion of the body, which can occur during thermal treatments, are alleviated.

Chemical strengthening generally relies on exchanging small ions in a glass surface by larger ions. The larger ions can be provided by treating the glass article in a molten salt bath. Substitution of larger for smaller ions in the glass surface tends to expand the glass structure, and this expansion is restricted by the glass interior. Consequently, the surface of the glass is placed in a state of compression, and a balancing tensile stress is generated in the interior. The successful use of chemical ion-exchange strengthening was first reported by Kistler in 1962 [3], and numerous papers have been published since then, as reviewed recently by Bartholomew and Garfinkel [4], and Donald [5]. The mechanism of ion-exchange depends on the diffusivity of the respective ions, and the highest diffusivities are generally found for alumino-silicate compositions. These glasses, therefore, provide the most useful materials by yielding compressive layers of practical thicknesses in realistic treatment times.

Using, for example, a lithium alumino-silicate composition, Li^+ ions near the glass surface may be replaced by larger Na^+ ions from a sodium salt bath, e.g. $NaNO_3$. Similarly, for sodium alumino-silicate glasses, Na^+ would be replaced by larger K^+ ions from a potassium salt bath. Numerous other ion-exchange treatments have been investigated [5], including exchange of Na^+ or K^+ for Rb^+, Cs^+, Ag^+, Cd^{2+} or Zn^{2+}. Because ion-exchange is a diffusion-controlled process, it is temperature and

0022-2461/88 $03.00 + .12

TABLE I Glass batch constituents

1. Li_2O	BDH, GPR Li_2CO_3
2. Na_2O	BDH, GPR anhydrous Na_2CO_3
3. MgO	BDH, GPR MgO
4. Al_2O_3	BDH, AR Al_2O_3
5. B_2O_3	M & B Laboratory Chemicals H_3BO_3, and/or BDH, AR $Na_2B_4O_7 \cdot 10H_2O$
6. P_2O_5	Koch-Light, pure $AlPO_4 \cdot 3H_2O$
7. SiO_2	Tilcon L30A low-iron silica sand

TABLE II Compositions of glasses employed in present work (mol %)

Glass code	Li_2O	Na_2O	MgO	B_2O_3	Al_2O_3	P_2O_5	SiO_2
A	29.60	–	9.96	–	9.90	1.15	49.39
B	30.30	–	8.12	–	10.11	1.19	50.28
C	20.76	4.82	10.35	2.43	10.29	–	51.35
D	17.68	4.26	10.92	3.79	11.51	1.03	50.81
E	17.86	4.31	11.03	3.84	11.63	–	51.33
F	18.72	2.26	19.42	1.20	10.42	0.98	47.00

time dependent. Consequently, the higher the ion-exchange temperature, the shorter is the time required to develop a compressive layer. The upper temperature is limited, however, due to the possibility of stress relaxation (if ion-exchange is carried out at temperatures approaching or exceeding T_g, the stresses generated by the process are quickly relaxed or eliminated by viscous flow of the glass). Ion-exchange times may vary from a few minutes to several hundred hours, depending on the glass composition, the temperature of the bath, and the depth and magnitude of compressive layer required. A prerequisite for an ion-exchange medium is, of course, that it must not chemically corrode the glass surface at the temperature employed.

Very high mechanical strengths can be achieved using the chemical ion-exchange strengthening method, with some reports of materials exhibiting strengths in bending of up to around 800 MPa [6–8]. This is nearly an order of magnitude higher than for untreated glass, and is a direct consequence of the need to overcome this compressive stress during external stressing of the glass, before the strength-impairing effects of surface defects become significant.

The thickness of the compressive layer may vary from a few micrometres to several hundred micrometres, depending on the precise glass composition, treatment conditions and glass thickness. If the layer is very thin or the glass article relatively thick, the maximum balancing internal tensile stress may be very small so that, unlike thermally strengthened glasses, these materials can be cut or machined after treatment. On the other hand, with thicker compressive layers and thin glass articles, the internal tensile stress may be above that required for crack branching so that when fracture is initiated, by penetration of a crack through the compressive layer, a large number of small, approximately equi-sized glass fragments is produced. This phenomenon has given rise to the special class of chemically strengthened materials, the frangible or "command-break" glasses [9].

The stress profile of chemically strengthened glasses is an important property which controls not only the ultimate strength of the material, but also the way in which it fractures. Stress profiles may be measured by conventional photo-elastic methods [10], by the scattered light technique [10, 11], or by progressively removing surface layers by etching and then measuring the resultant dimension changes [12]. An alternative method, more suited to the measurement of stress profiles in thin chemically strengthened glasses where stress gradients are high, has been developed recently by Bradshaw [13]. This method combines the scattered light technique with etching, and is described in more detail later.

The present paper describes work carried out on a number of lithium alumino-silicate glasses containing MgO, Na_2O, or P_2O_5 additions. Stress profiles and mechanical properties have been monitored for these materials as a function of treatment conditions, and these data are reported and discussed.

2. Experimental procedures

2.1. Preparation of glass samples

Glass batch materials were prepared, using the constituents summarized in Table I, by tumbling the appropriate powders, calculated to yield 500 g samples of glass, for 1 h in polyethylene bottles. These batches were then melted in air in a closed Pt/5% Rh crucible at a maximum temperature of 1500° C for 3 to 5 h. Good homogeneity was achieved by quenching the molten glass into distilled water, which produced a granulated product, followed by re-mixing and re-melting the product, this procedure being carried out twice. Details of the glass compositions prepared are given in Table II. These are nominal compositions. Weight losses during melting were generally < 0.5 wt %.

Molten glass was subsequently cast into pre-heated (to 450° C) 38 mm diameter cylindrical graphite moulds to give solid glass cylinders approximately 80 mm high. These cylinders were immediately annealed for 1 h, and then furnace cooled (at approximately $0.5° \mathrm{C\,min^{-1}}$) to room temperature. The annealing temperature employed for each glass composition was based on prior knowledge of T_g, as determined by differential thermal analysis at a heating rate of $10° \mathrm{C\,min^{-1}}$ (Stanton Redcroft DTA Model 674).

Disc samples 1.3 to 1.4 mm thick were then cut from these cylinders, employing a diamond wheel. The discs were subsequently cleaned ultrasonically in dichloromethane and iso-propanol, and allowed to dry under an infrared lamp. They were then etched in an aqueous solution of 10% HF and 6% H_2SO_4 in order to remove machining damage and to thin the samples down to a standard thickness of 1.15 to 1.25 mm. After re-drying, the disc samples were weighed to an accuracy of 0.0001 g, and then treated in molten $NaNO_3$ (BDH Analar grade), contained in a 1 litre capacity stainless steel beaker, for various lengths of time at 385 ± 2° C. A maximum of 24 samples could be treated at any one time.

The weight change/unit area was derived for each disc sample by weighing and micrometric measurements.

2.2. Mechanical property measurements

As-prepared disc samples (38 mm diameter) were covered in polyethylene tape, in order to retain the small fragments of glass on fracture, and tested in biaxial flexure, using a loading rate of 0.75 mm min^{-1}. The piston-on-three-ball method was employed [14–17], with a ball separation of 22 mm and a piston diameter of 2.4 mm. This method requires a knowledge of Poisson's ratio for the material tested. A standard value of 0.24 was taken for all the glasses investigated in this work.

2.3. Stress profile measurements

Stress profiles were measured using the scattered light and etching technique, as described by Bradshaw [13]. This method involves the scattering of light from a finely collimated laser beam passed through the central plane of the sample and plane polarized at 45° to the plane of the sample. Due to the birefringence of the glass when stressed, this beam splits into two components and gives rise to interference fringes when viewed at 45° to the surface of the glass. From a knowledge of the fringe separation and the stress optical coefficient of the glass, a value for the centre tension can be derived [13]. The glass is then etched in an aqueous solution of 10% HF and 6% H_2SO_4 to remove some of the surface. After removal of a thin surface layer, the new centre tension is measured. This process is then repeated a number of times until zero centre tension is achieved. The stress profile is subsequently derived from the relationship between the thickness change and centre tension change.

This method was used to measure the stress profiles of a selection of glass samples of different compositions employed in the present work. A Spectra-Physics Model 106-1 He–Ne gas laser with a power output of 10 mW was utilized. The initial and final thickness of each glass sample was measured to an accuracy of $\sim 1\,\mu$m using a micrometer. Some intermediate values were also measured after various stages of etching. The precise thickness changes after each etching treatment were then determined from a knowledge of the specimen weight change as a function of thickness change. A standard value of 2.75 nm mm^{-1} MPa^{-1} was taken for the stress optical coefficient of the glasses studied in the present work [13, 19]. The computed stress profiles were subsequently normalized to a standard glass thickness of 1.20 mm to enable direct comparison between samples of slightly different thicknesses. As a check on the overall technique, the centre tension of a sample of Corning Glass Works chemically strengthened glass, Code 0319, was also measured in the present work, and compared with the earlier results of Bradshaw [13].

3. Results

3.1. Thermal properties of glasses

The thermal properties of the glasses, designated compositions A to F, are given in Table III. Compositions A and B exhibited a single, sharp crystallization peak at around 700° C, whilst glass F had a single broad peak centred around 770° C. Compositions C, D and E exhibited less well-defined crystallization features. All the glasses showed well-defined T_gs and melting ranges. Representative DTA traces for these glasses are shown in Fig. 1.

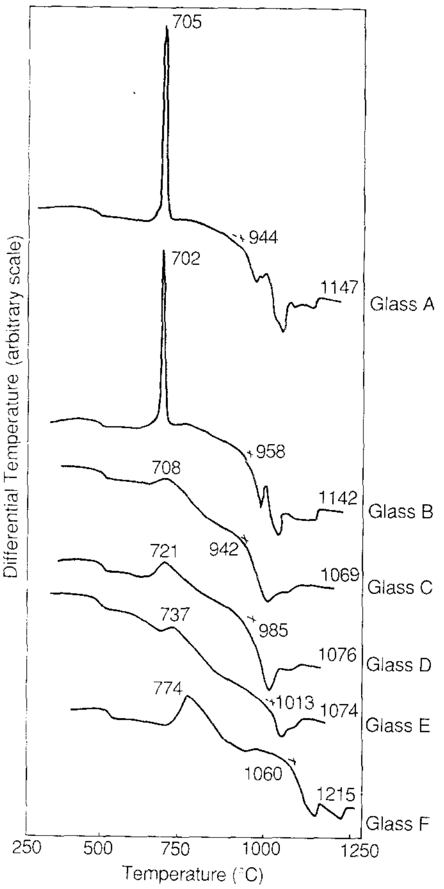


Figure 1 Differential thermal analysis traces obtained at a heating rate of 10° C min^{-1} for the glasses investigated.

3.2. Ion-exchange data

The change in weight (which is a measure of the uptake of Na^+ ions) as a function of treatment time for the six glass compositions studied is given in Table IV. Each measurement is the mean taken from a minimum of eight samples. The results are also shown graphically for glass A in Fig. 2, with the weight increase plotted as a function of (time)$^{1/2}$. A strong linear dependence is noted.

3.3. Stress profiles

The centre tension for Corning Code 0319 chemically strengthened glass 1.25 mm thick, as determined by the present method, was found to be 100 MPa. This value agrees closely with the earlier results of Bradshaw [13].

Stress profiles for a number of the present glasses treated for 49 h are shown in Figs 3 to 8. A summary of the important parameters is given in Table V.

Compositions A and B (Figs 3 and 4) exhibited an unusual stress profile where the outermost layers of the glass were in tension, rather than the more usual compression. This tensile zone extended ~ 20 to $30\,\mu$m into the surface; for depths greater than this the stress then became compressive. After reaching a maximum compressive stress, the magnitude of the

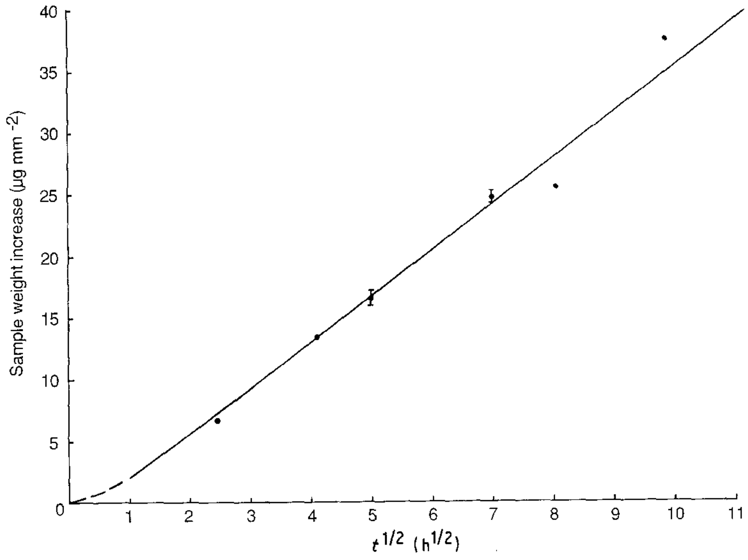


Figure 2 Weight increase of composition A as a function of treatment (time)$^{1/2}$ (in molten sodium nitrate at 385° C).

compressive stress decreased with further increase in depth, finally becoming tensile again, thus leading to the normal internal tension associated with chemically strengthened glasses.

The other glasses generally exhibited normal, "relaxed" stress profiles (Figs 5 to 8), for which the maximum value of compressive stress was found just under the surface, rather than at the surface. The highest compressive stress was noted for composition F (570 MPa), whilst the lowest was found for B (250 MPa). The value for centre tension was similar for compositions A to E (80 to 100 MPa), but was lower for composition F (75 MPa); this latter composition also exhibited the thinnest compressive layer (110 µm compared to 170 to 270 µm for the other glasses).

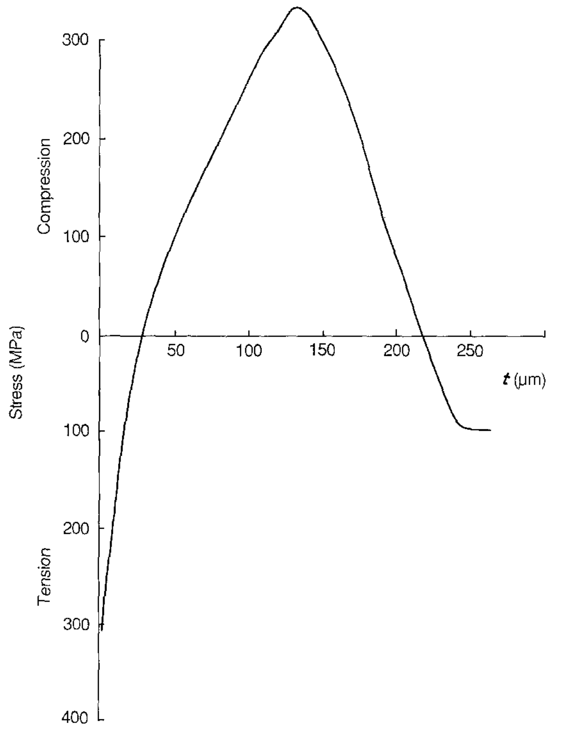


Figure 3 Stress profile of composition A ion-exchanged for 49 h in sodium nitrate at 385° C.

3.4. Mechanical properties

The biaxial flexure strength of the discs is summarized in Table VI for each glass composition and treatment time. The results are also shown graphically for composition A in Fig. 9.

For composition A, a maximum in strength was obtained corresponding to a treatment time of around 6 h. For treatment times in excess of 6 h, the strength decreased slowly. For example, treatment for 97.5 h yielded samples which were only about 70% as strong as samples treated for 6 h.

The strongest materials were obtained for those compositions which contained Na_2O in the starting glasses. Comparing the results for the different glasses (Table VI), compositions C, D and E, which contained 4 to 5 mol % Na_2O, had strengths in excess of 500 MPa for a standard treatment time of 49 h. This compares with a strength of around 380 MPa for glass A, treated for an equivalent time. The strongest material, however, was found for glass F which, in addition to containing some Na_2O, also contained a

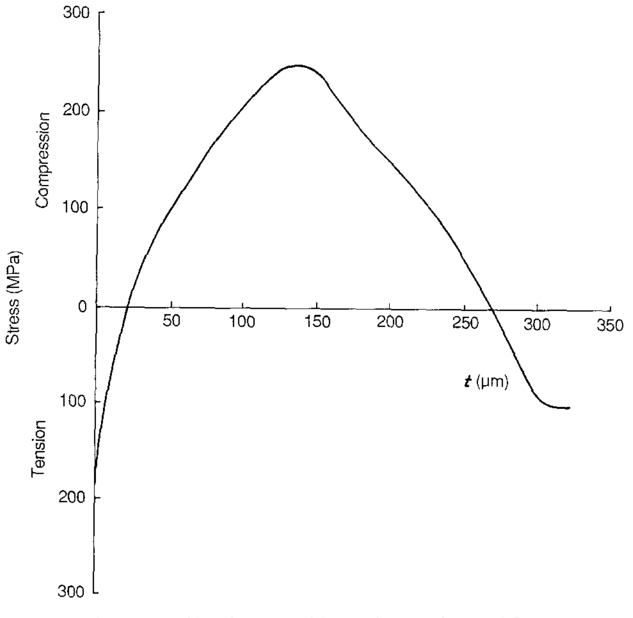


Figure 4 Stress profile of composition B ion-exchanged for 49 h.

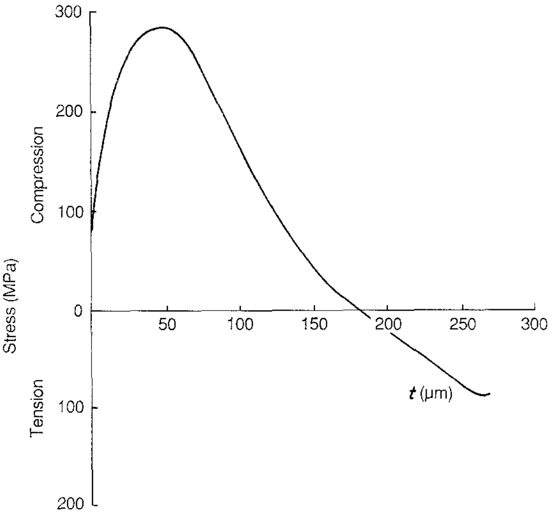


Figure 5 Stress profile of composition C treated for 49 h.

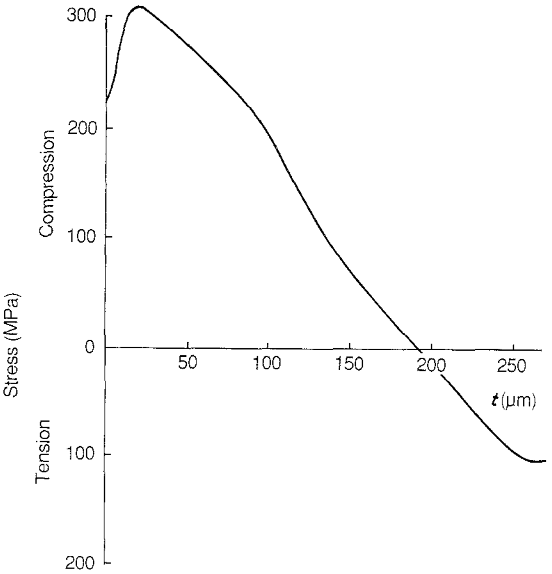


Figure 6 Stress profile of composition D treated for 49 h.

higher concentration of MgO than the other glasses studied. A very high strength of 860 MPa was observed for this material, treated for 49 h.

Photographs of samples fractured in biaxial flexure are shown in Figs 10 to 15. These illustrate the variation in franged particle size and shape with treatment conditions and composition. In Figs 10a to f, the variation is shown as a function of treatment time, for composition A, ranging from 6 h (a) to 97.5 h (f). Radial cracking, emanating from the fracture origin, is noted in Fig. 10a, with very little circumferential cracking being apparent. As the treatment time increased, the number of radial and circumferential cracks increased significantly, leading to approximately equi-axed and equi-sized particles for times in excess of 25 h. As the treatment time was increased further, the franged particle size decreased, until at 97.5 h particles < 1 mm in size were obtained. Figs 11 to 15 show the effect of composition on the fracture behaviour, for a standard treatment time of 49 h. It can be seen that composition B gives the smallest franged particle size for this treatment. The particle size for the glasses follows the series, E > C > F > D > A > B.

4. Discussion

4.1. Ion-exchange

The alkali ion-exchange process is a diffusion-controlled reaction, following Fick's Second Law (the reaction rate is proportional to $(\text{time})^{1/2}$), as illustrated in Fig. 2 for composition A.

4.2. Stress profiles

All of the glasses studied, with the exception of composition F, exhibited a "relaxed" stress profile where the maximum value of compressive stress is obtained not at the surface, but at some distance within the glass interior (Figs 3 to 8). This effect has been noted previously for both sodium alumino-silicate [13] and lithium alumino-silicate [18, 19] systems. It is attributed to the effects of thermal stress-relaxation of the glass when treatment is carried out at temperatures of the order of 100° C or less below the strain point of the glass [18, 19].

Two of the compositions studied (A and B), were observed to exhibit very unusual stress profiles for which the glass surface itself was in tension, rather than in compression (Figs 3 and 4). The magnitude of the tension in the surface was high enough to cause fracture and crazing of the immediate surface layers, which can be seen optically under suitable lighting conditions, as shown in Fig. 16 for a small plate of glass B. The tensile layer extends approximately 20 to 30 μm into the glass interior (Figs 3 and 4). At depths

TABLE III Thermal properties of glasses*

Glass code	T_g (° C)	T_{xp} (° C)	T_{ms} (° C)	T_{liq} (° C)
A	499 ± 4	705 ± 4	944 ± 3	1147 ± 10
B	502 ± 4	702 ± 3	958 ± 7	1142 ± 3
C	508 ± 2	708 ± 4	942 ± 5	1069 ± 9
D	515 ± 4	721 ± 16	985 ± 19	1076 ± 6
E	510 ± 4	737 ± 7	1013 ± 2	1074 ± 2
F	541 ± 4	774 ± 3	1060 ± 12	1215 ± 3

*T_g = glass transition temperature, T_{xp} = crystallization peak temperature, T_{ms} = temperature corresponding to the extrapolated start of melting (defined in Fig. 1), T_{liq} = liquidus temperature (end of melting range).

TABLE IV Sample weight increase as a function of treatment time in sodium nitrate at 385° C

Glass code	Time of treatment (h)	Sample weight increase ($\mu g\,mm^{-2}$)
A	6	6.7 ± 0.1
A	17	13.4 ± 0.2
A	25	16.5 ± 0.6
A	49	24.9 ± 0.4
A	65	25.4 ± 0.1
A	97.5	37.7 ± 0.2
B	49	33.1 ± 0.8
C	49	10.6 ± 0.1
D	49	13.6 ± 0.2
E	49	9.0 ± 0.2
F	49	7.8 ± 0.3

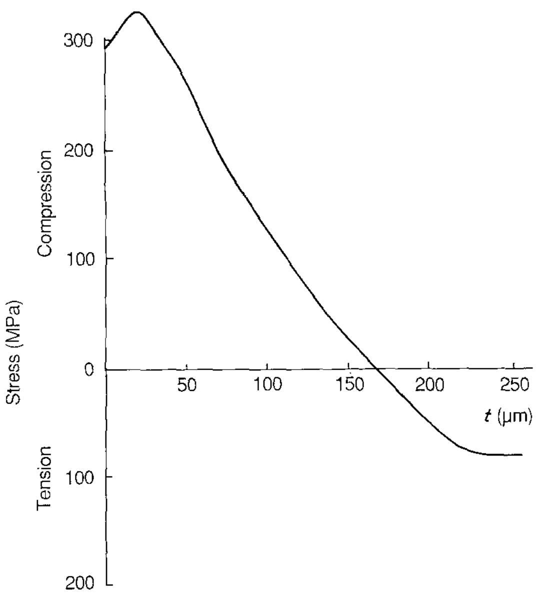


Figure 7 Stress profile of composition E treated for 49 h.

greater than this, the stress becomes compressive, and thereafter exhibits a normal, relaxed stress profile.

As far as the authors are aware, such an effect has not been reported previously for chemically strengthened glasses. Tensile stresses can, however, be induced into a glass surface by a chemical ion-exchange treatment in which small ions from an external source are exchanged for larger ions in the glass surface (the inverse of the normal chemical strengthening method). This phenomenon was first reported by Stewart and Young [20], and later by Ernsberger [21] as a mechanism for revealing the presence of surface flaws on glass. Failure of the glass surface, either during the ion-exchange treatment or later during tensile bending, leads to a crazed appearance, analysis of which can identify the origins and severity of the original flaws.

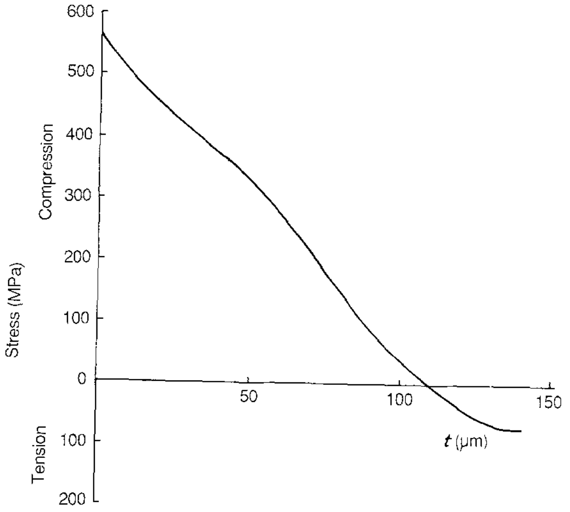


Figure 8 Stress profile of composition F treated for 49 h.

The origin of the thin tensile layer in the present examples is believed to arise from differences in thermal expansion between the bulk glass and the ion-exchanged layers, with the surface regions of the glass exhibiting a higher thermal expansion than that of the interior. (It is recognized that glasses containing more than one alkali species generally exhibit a maximum in thermal expansion with composition, due to the "mixed alkali" effect, e.g. [22]). On cooling from the treatment temperature, this effect would tend to place the outermost layers of the glass in tension, before the overriding influence of ion-exchange leads to a gradual transition from tension to compression as the distance from the surface increases.

Addition of Na_2O to the base glass (compositions C to F), which would be expected to increase the thermal expansion of the base glass in relation to the ion-exchanged composition, eliminates this thin tensile layer, and leads to a normal, relaxed stress profile (Figs 6 to 9). The precise cause of this effect is not easy to verify in practice, however, because the properties of an ion-exchanged surface layer may vary very significantly from the properties of a bulk sample prepared by normal fusion processes [23].

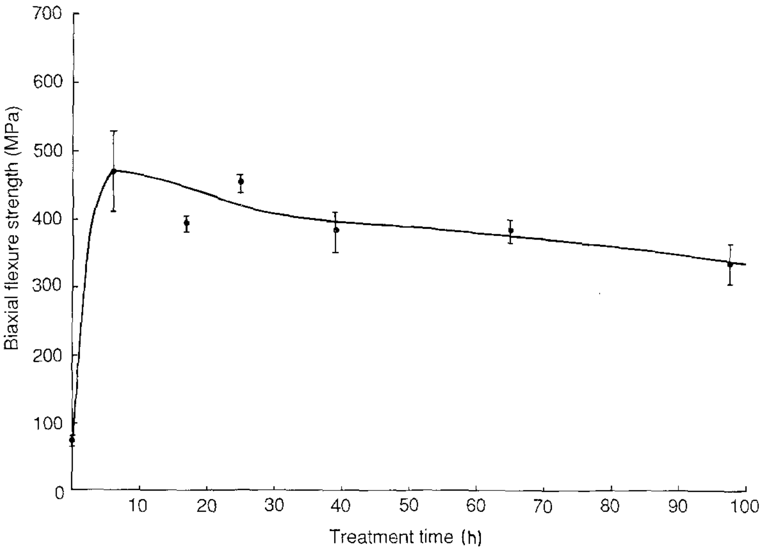


Figure 9 Biaxial flexure strength of composition A as a function of treatment time.

TABLE V Summary of stress profile data for samples treated for 49 h in sodium nitrate at 385° C

Glass code	Centre tension (MPa)	Surface compression (MPa)	Maximum compression (MPa)	Thickness of compressive layer (μm)
A	95	−310	330	220
B	95	−170	250	270
C	85	80	290	190
D	100	230	310	195
E	80	290	330	170
F	75	570	570	110

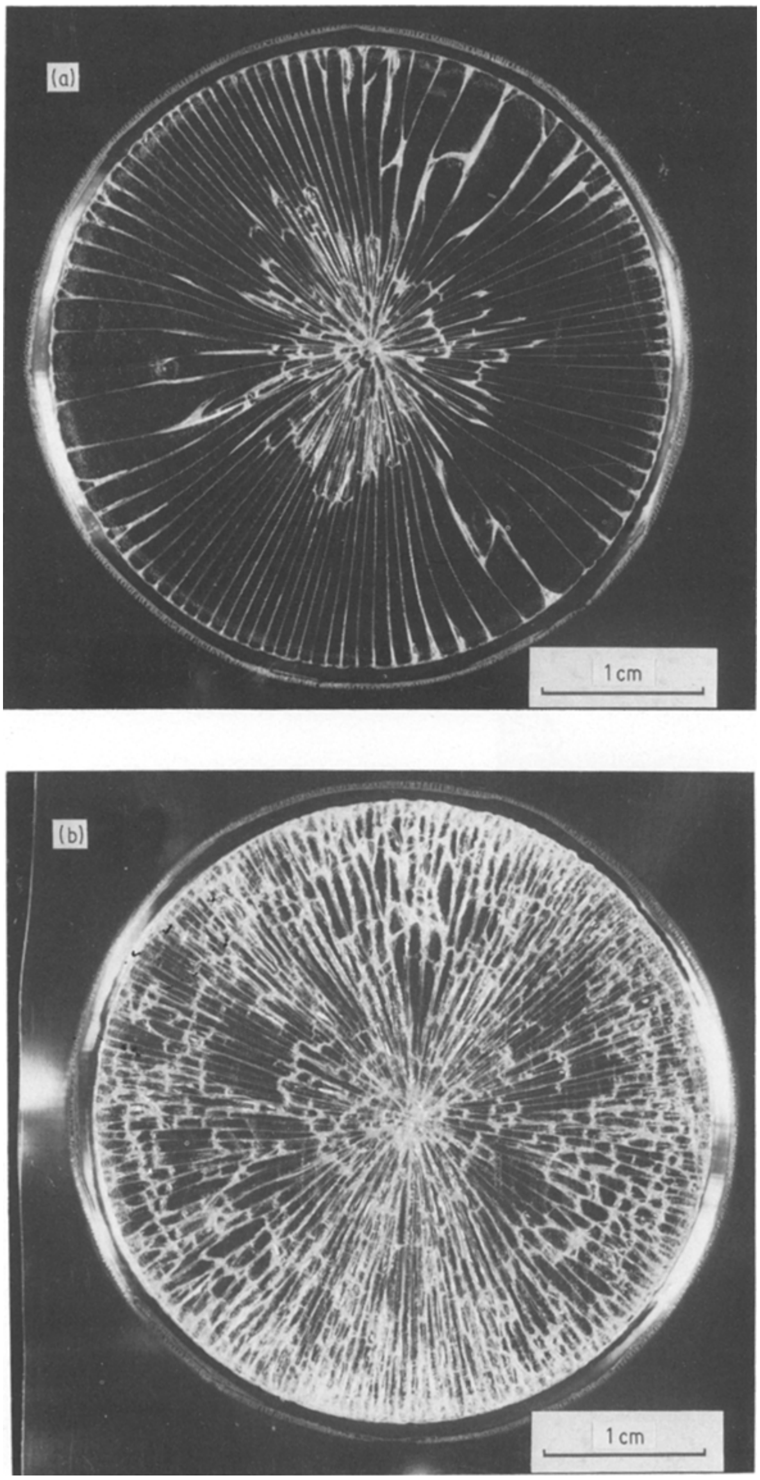


Figure 10 Samples of glass A fractured in biaxial flexure. (a) ion-exchanged for 6 h, (b) 17 h, (c) 25 h, (d) 49 h, (e) 65 h and (f) 97.5 h.

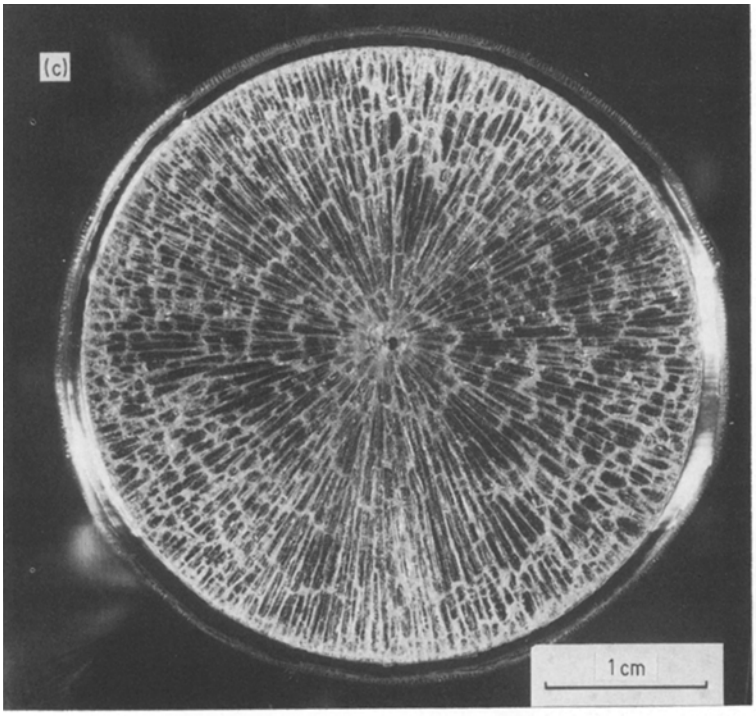
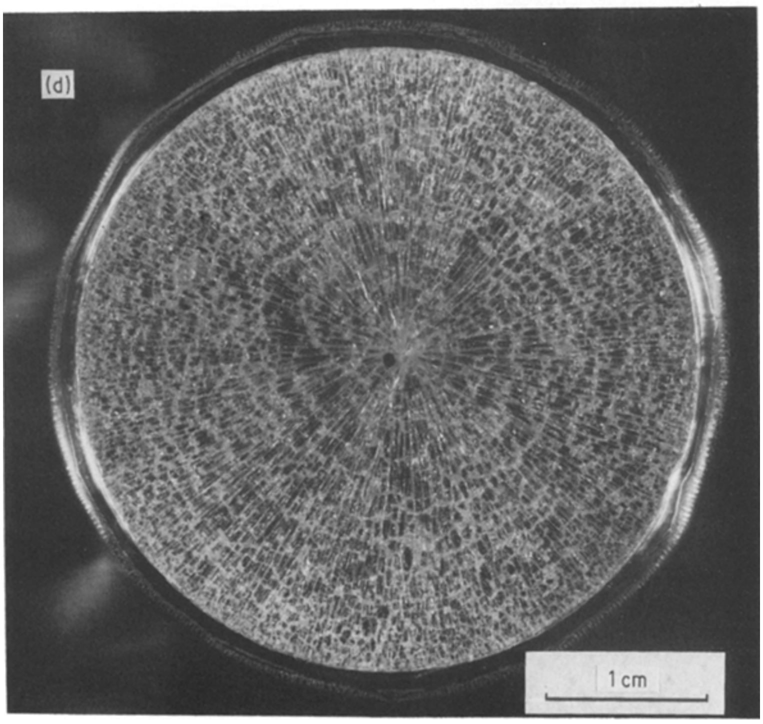


Figure 10 Continued

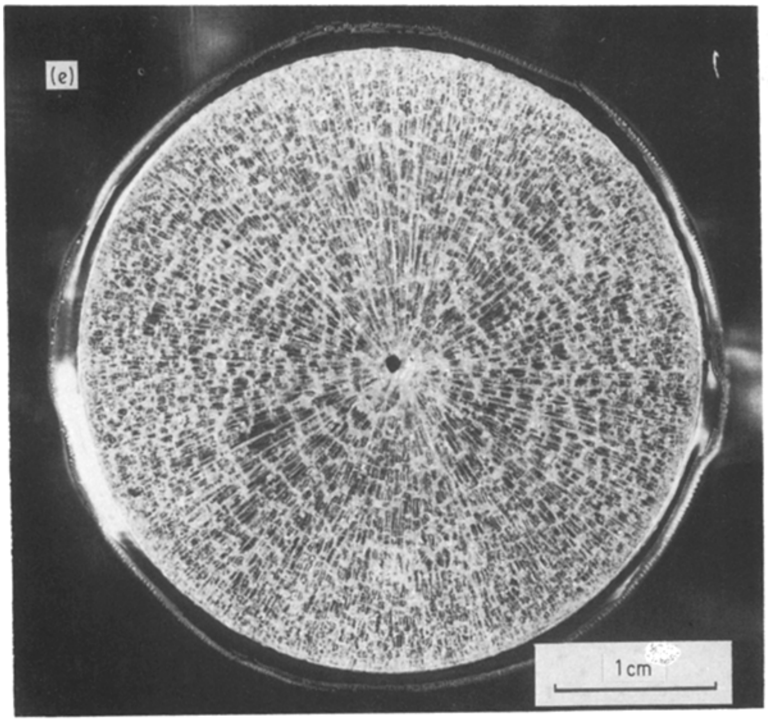


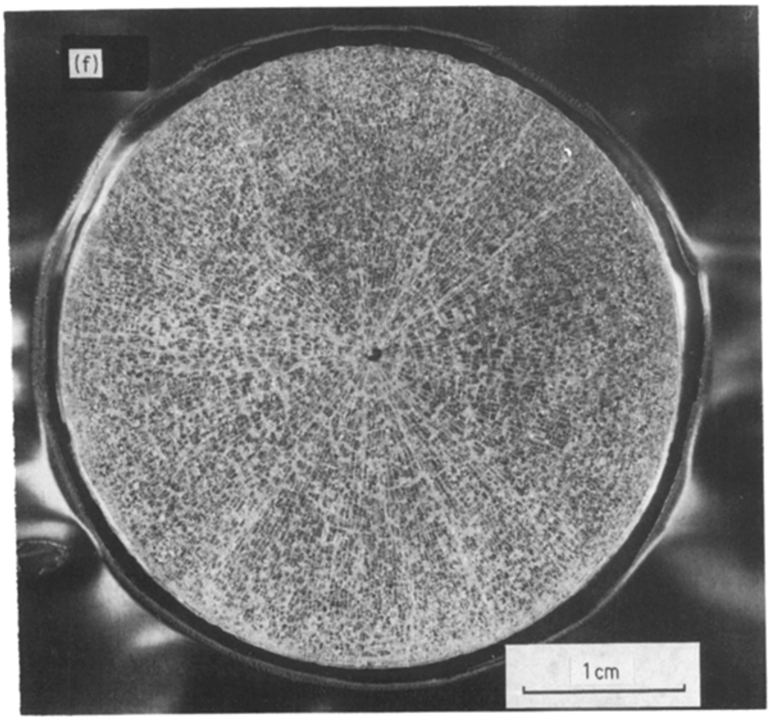
The effect of small additions of P_2O_5 on the resultant stress profiles is illustrated in Figs 5 and 6 for glasses D and E. The only difference between these two compositions is that glass D contains an addition of 1.03 mol % P_2O_5. This apparently gives rise to a deeper compressive layer (195 μm for D, compared to 170 μm for E). Correspondingly, a greater sample weight increase is noted for composition D (13.6 μg mm^{-2} compared to 9.0 μg mm^{-2} for glass E), as recorded in Table IV. A similar result, in which P_2O_5 enhances alkali diffusion, has been noted before [24, 25].

4.3. Mechanical properties

A maximum in strength as a function of treatment time is noted for composition A (Fig. 9). The falling off in strength with longer treatment times may be related to deep ion-exchange effects, although the precise mechanism is uncertain [26]. Alternatively, it may be associated with structural relaxation of the glass [6, 27, 28]. Fig. 17 illustrates clearly how the strength decreases with weight increase during treatment. The sample weight increase is related to the uptake of Na^+ ions and is expected, therefore, to be proportional to the ion-exchanged depth. It should be noted, however,

Figure 10 Continued





that the treatment that provides the strongest material in the short term is not necessarily the optimum for practical applications. This is because the compressive layer should be $> 50\,\mu m$ thick in order to make the glass reasonably resistant to the effects of accumulated surface damage.

With the thin samples employed in the present work, very small franged particle sizes are obtained for many of the treatments (Figs 10c to f, 11 to 15). This is due to the high internal tensile stresses generated during the ion-exchange process (Table V). The smallest franged particle size, for a given treatment (49 h at 385° C), occurs for compositions B and A which have the highest Li_2O content of the glass series. Composition D which contains some P_2O_5 also gives a slightly smaller particle size than do compositions C and E which do not.

Some very strong materials have been successfully prepared in the lithium magnesium alumino-silicate system. Composition F, for example, exhibits a biaxial flexure strength of 860 MPa, whilst compositions C, D and E exhibit strengths in excess of 500 MPa. This, in combination with the relatively low melting temperatures (Table III) and ease of preparation of these

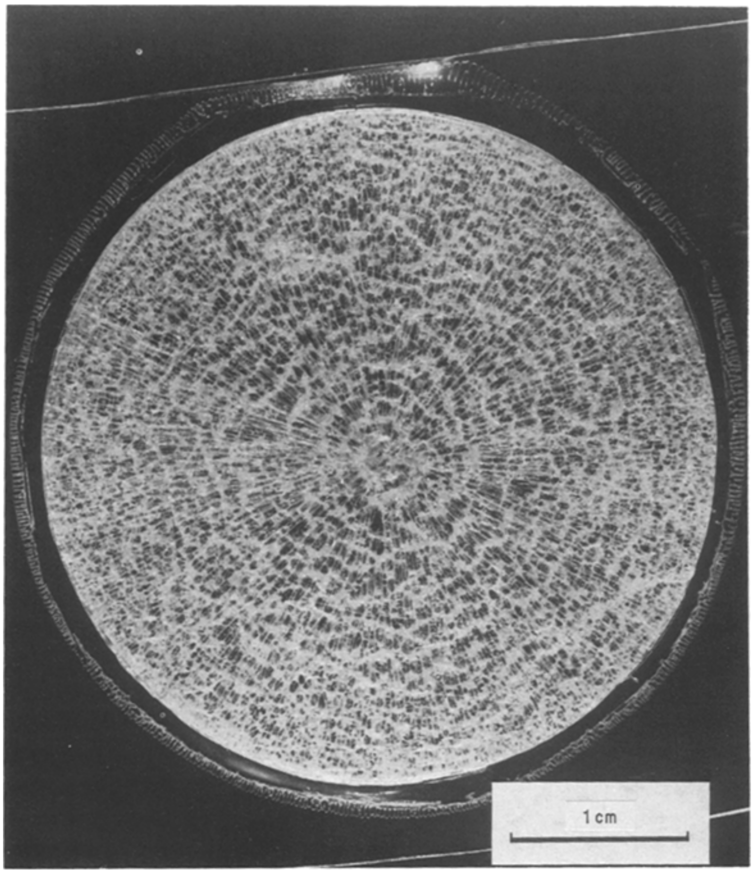


Figure 11 Sample of glass B ion-exchanged for 49 h and fractured in biaxial flexure.

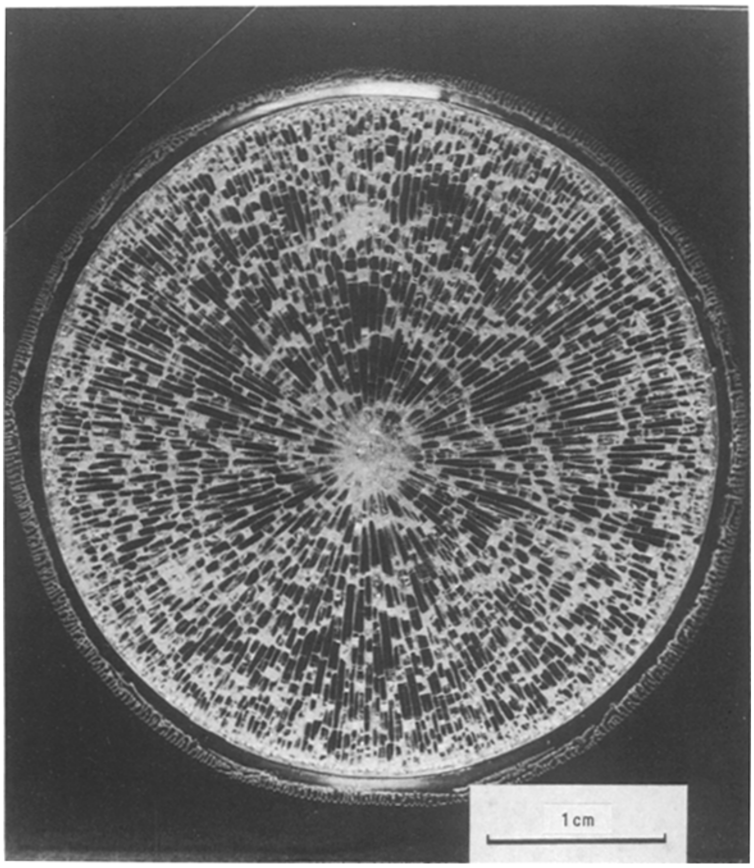


Figure 12 Sample of C treated for 49 h and fractured in biaxial flexure.

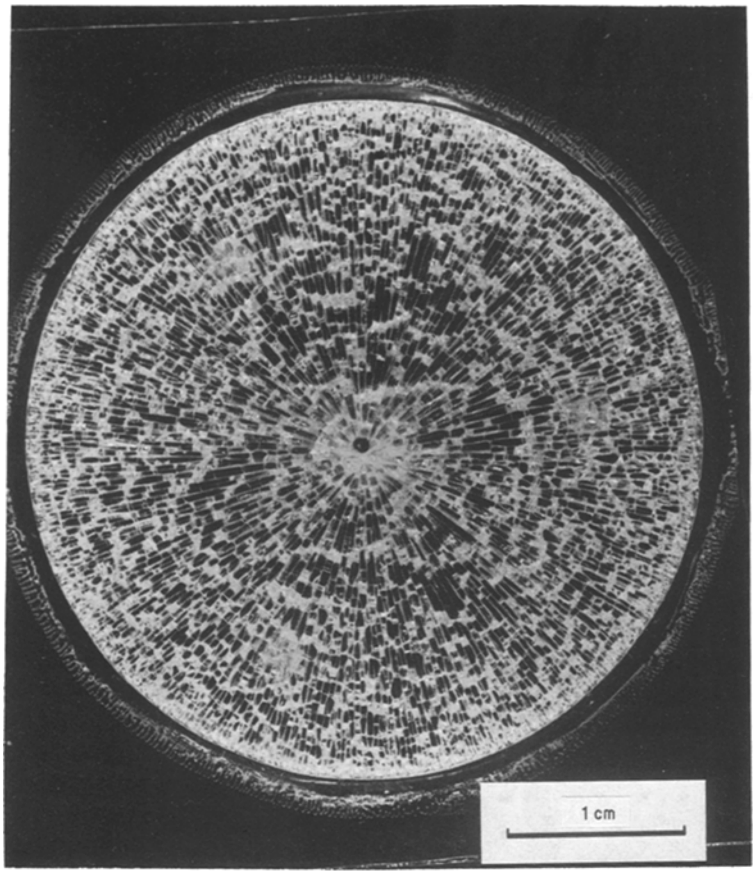


Figure 13 Sample of D treated for 49 h and fractured in biaxial flexure.

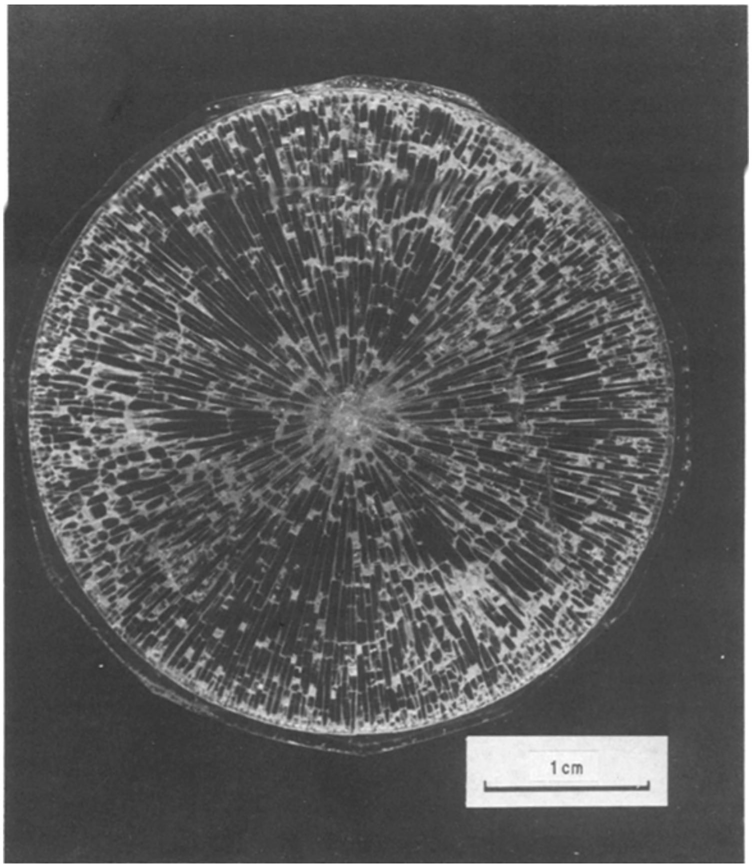


Figure 14 Sample of E treated for 49 h and fractured in biaxial flexure.

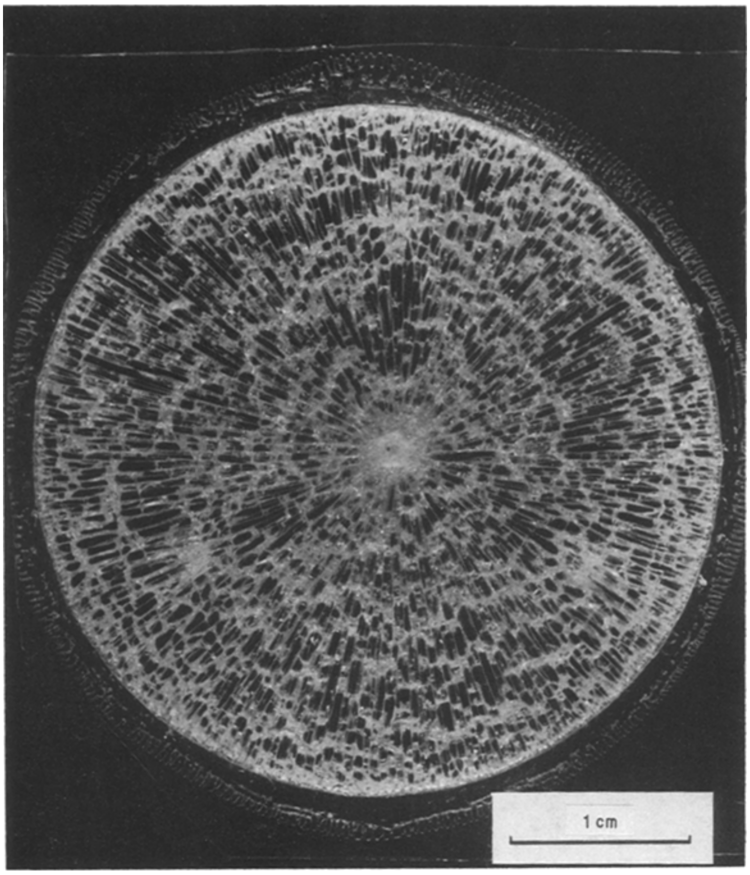


Figure 15 Sample of F treated for 49 h and fractured in biaxial flexure.

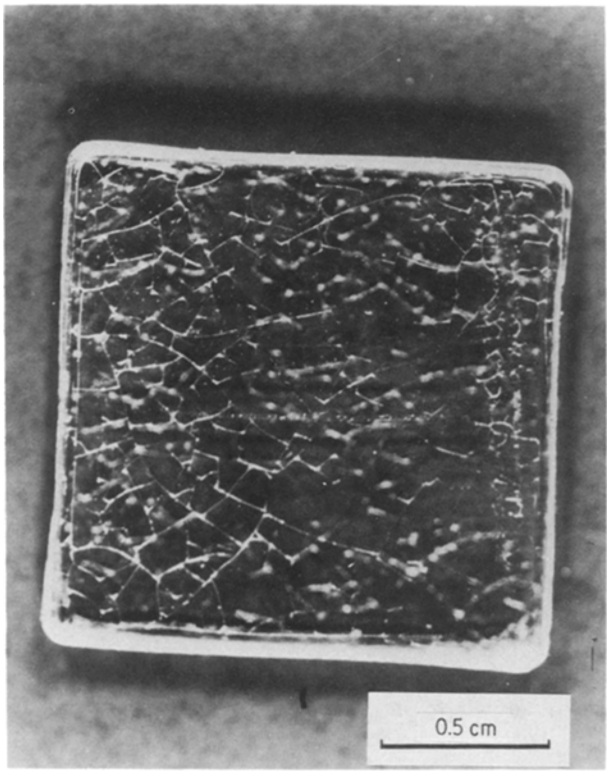


Figure 16 Sample of composition B ion-exchanged for 49 h, showing crazing of the glass surface due to the effect of tension in the surface.

glasses, makes them attractive for the preparation of high-strength materials.

Further work is underway on the static fatigue resistance and chemical durability of these glasses, and the results will be reported at a later date.

5. Conclusions

1. A number of chemically strengthened lithium magnesium alumino-silicate glasses have been prepared by ion exchange in sodium nitrate at 385° C.

TABLE VI Biaxial flexure strength as a function of treatment time in sodium nitrate at 385° C

Glass code	Treatment time (h)	Biaxial flexure strength (MPa)
A	0	74 ± 6
A	6	470 ± 58
A	17	396 ± 10
A	25	454 ± 16
A	49	383 ± 31
A	65	386 ± 15
A	97.5	336 ± 28
B	49	309 ± 12
C	49	503 ± 65
D	49	516 ± 71
E	49	574 ± 73
F	49	858 ± 85

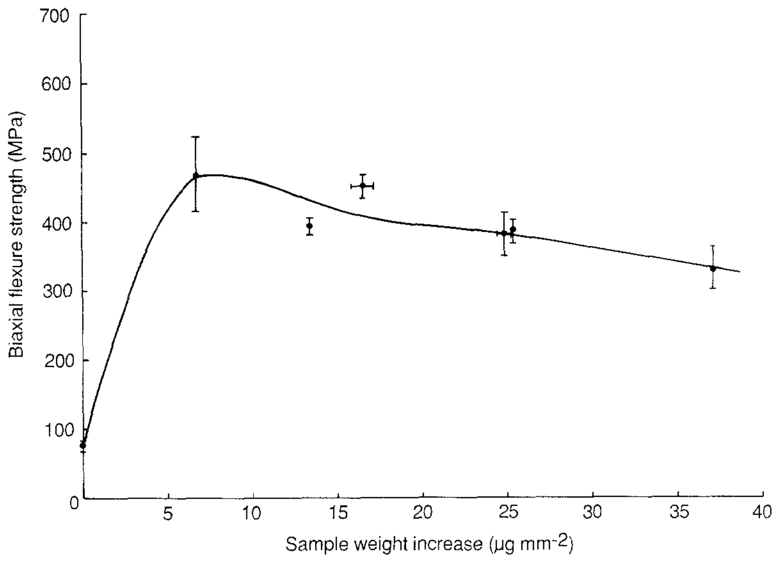


Figure 17 Strength of sample A as a function of sample weight increase during ion-exchange treatment.

2. The increase in weight of the treated samples (which is a measure of the uptake of Na^+ ions) follows a $(time)^{1/2}$ diffusion law.

3. The strength of one of the compositions (A) has been found to peak after around 6 to 10 h treatment time. Prolonged treatment to 97.5 h results in a reduction in strength to around 70% of the corresponding 6 h value. This fall-off in strength is most probably associated with stress-relaxation effects.

4. The strongest material (tested in the as-treated condition) is composition F, which exhibits a biaxial flexure strength of around 860 MPa.

5. Two of the compositions (A and B) exhibit an unusual stress profile where the outermost layers of the surface are in tension, rather than compression. This stress is high enough to cause localized failure of the glass surface, which leads to a surface crazing effect. The effect is probably associated with the influence of differential thermal expansion between the ion-exchanged and bulk glasses.

6. The effect noted in (5) is eliminated for compositions which contain some Na_2O in the untreated glass (compositions C to F). After treatment, these glasses exhibit normal, relaxed stress profiles.

7. Small additions of P_2O_5 appear to enhance ion exchange and lead to a higher weight uptake and a deeper compressive layer for a given glass composition.

Acknowledgements

The authors wish to thank Mr W. Bradshaw, AWE, for useful discussions, including advice on the stress-profile measurements. This paper is published by permission of the Controller, HMSO, holder of Crown Copyright.

References

1. P. WARD and G. M. BALLARD, US Patent 4205976 (1980).
2. R. GARDON, in "Glass Science and Technology", Vol. 5, edited by D. R. Uhlmann and N. J. Kreidl (Academic, New York, 1980) pp. 145–216.
3. S. S. KISTLER, *J. Amer. Ceram. Soc.* **45**(2) (1962) 59.
4. R. F. BARTHOLOMEW and H. M. GARFINKEL, in "Glass Science and Technology", Vol. 5, edited by D. R. Uhlmann and N. J. Kreidl (Academic, New York, 1980) pp. 217–70.
5. I. W. DONALD, "Inorganic glasses and glass-ceramics: a review", AWRE Report No. 0 19/84 (HMSO, London, 1984).
6. M. E. NORDBERG, E. L. MOCHEL, H. M. GARFINKEL and J. S. OLCOTT, *J. Amer. Ceram. Soc.* **47**(5) (1964) 215.
7. J. CORNELISSEN and A. J. BURGGRAAF, in Proceedings of the 7th International Conference on Glass (Gordon and Breach, New York, 1965) pp. 319.1–319.4.
8. M. ABOU-EL-LEIL and A. R. COOPER, *Glass Technol.* **21**(1) (1980) 57.
9. Anon., *Bull. Amer. Ceram. Soc.* **54** (1975) 19.
10. A. KUSKE and G. ROBERTSON, "Photoelastic Stress Analysis" (Wiley, London, 1974).
11. R. WELLER, *J. Appl. Phys.* **10** (1939) 266.
12. H. P. STEPHENS and E. K. BEAUCHAMP, *Bull. Amer. Ceram. Soc.* **53** (1974) 159.
13. W. BRADSHAW, *J. Mater. Sci.* **14** (1979) 2981.
14. F. F. VITMAN and V. P. PUKH, *Ind. Lab.* **29** (1963) 925.
15. J. B. WACHTMAN, W. CAPPS and J. MANDREL, *J. Mater.* **7** (1972) 118.
16. "Standard Test Method for Biaxial Flexure Strength of Ceramic Substrates", ASTM F 394-78 (1978) pp. 802–8.
17. J. E. RITTER, K. JAKUS, A. BATAKIS and N. BANDYOPADHYAY, *J. Non-Cryst. Solids* **38**, **39** (1980) 419.
18. W. J. SPOOR and A. J. BURGGRAAF, *Phys. Chem. Glasses* **7**(5) (1966) 173.
19. A. L. ZIJLSTRA and A. J. BURGGRAAF, *ibid.* **1** (1969) 163.
20. O. J. STEWART and D. W. YOUNG, *J. Amer. Ceram. Soc.* **57** (1935) 695.
21. F. M. ERNSBERGER, *Proc. Roy. Soc.* **A257** (1960) 213.
22. J. O. ISARD, *J. Non-Cryst. Solids* **1** (1969) 235.
23. A. J. BURGGRAAF, *Phys. Chem. Glasses* **7** (1966) 169.
24. Pittsburgh Plate Glass Co., Brit. Pat. 1071351 (1967).
25. D. W. RINEHART, US Pat. 4055703 (1977).
26. C. K. SAHA and A. R. COOPER, *J. Amer. Ceram. Soc.* **67** (1984) C-160.
27. P. ALOQUE and J. TOCHON, "Symp. sur la resistance mechanique du verre", Florence, Italy, September 1961 (Union Scientifique Continentale du Verre, Charleroi, Belgium, 1962) pp. 687–704.
28. J. B. WARD, B. SUGARMAN and C. SYMMERA, *Glass Technol.* **6** (1965) 90.

*Received 13 August
and accepted 1 December 1987*