Stress Relaxation in an Ion Exchanged Glass

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ABSTRACT. A field assisted ion exchanged soda-lime silicate glass tubes were soaked in a molten bath of potassium nitrate at different temperatures and different times. An attempt was made to study the effect of these parameters on the residual stress profiles. The residual stress arising due to a singly and doubly ion exchange at two different temperatures was examined. The results are discussed on the basis of the stress relaxation and ionic diffusion.

Typically in electric field assisted ion exchange strengthening of glass (Weber 1965, Ohta and Hara 1970, Abou-El-Leil and Copper 1978, 1979), a dc field is applied in some direction to enhance exchange of potassium (K^+) ions from a molten salt with sodium (Na^+) ions in a glass (single ion exchange). To achieve ion exchange at both surfaces of the glass (double ion exchange), the field direction must be reversed after exchanging one surface. A 'doubly exchanged layer' is produced near the surface where some of the initially introduced K^+ ions have been replaced by Na^+ ions.

Besides the use of field assisted ion exchange as a glass strengthening process, it has been used to develop the refractive index gradient for optical waveguides and to improve the corrosion resistance of the glass.

For studying stress relaxation during field assisted ion exchange, knowledge was required to the stresses in an ion exchanged glass as a function of exchange temperature and time as reported by Shaisha and Cooper (1981). In the present work, the effect of ordinary ion exchange (electric field is off) after field assisted ion exchange on the stress relaxation was studied.

Generation and Relaxation
of
Residual Stresses

The residual stress built up from the ion exchange process could be envisaged as follows. To begin with, it must be recognized that in a soda-lime-silica glass, Na^+ ions occupy sites that need be similar. On the basis of a random network model, it is reasonable to expect a distribution of sites whose size varies about some mean value. Therefore, when the Na^+ ions in the surface are replaced by the K^+ ions, they need not occupy exactly the same positions as those occupied by Na^+ ions. Some ions could occupy positions somewhat larger than the average, thereby reducing the strain energy and yet preserving an electrical neutrality. Since the size of K^+ ions (radius 1.33 Å) is greater than that of Na^+ ions (radius 0.98 Å), the structure would tend to expand in all directions to accommodate larger K^+ ions. This expansion along the axial direction is prevented by the unexchanged part of the glass due to the plane strain condition. This phenomenon gives compressive stress ($\sigma_{\theta\theta}$ and σ_{zz} in the glass tube) due to the high internal pressure caused by the K^+ ions. The resulting displacement is attenuated between the first (oxygen ions directly surrounding the K^+ ion) and second shells as part of the volume expansion is taken up by the free volume round the first shell.

However, during ion exchange, other processes affect the value of the stress, the most important of these are the stress relaxations resulting from shear viscous flow and diffusional considerations. The higher the temperature of the exchange, the lower the viscosity and hence the greater will be the effect of stress relaxation owing to flow. Diffusional relaxation is an unavoidable process which will decrease the surface compression. For a diffusion-controlled process (surface concentration constant for all times of exchange), just after the exchange begins the concentration gradient is at its steepest and the surface compression at its maximum. The concentration gradient decreases and eventually disappears if the exchange is carried out long enough. Therefore, the surface compression decreases to zero, when there is no longer a gradient.

Stress Measurements

A ring sliced from the middle portion of the tube was ground using 400-grit sic paper and then polished with diamond compound. Optical retardation was determined by reading a Berek compensator using a polarizing microscope, it was then converted into the stress difference ($\sigma_{\theta\theta}-\sigma_{rr}$) using the stress optical coefficient of the value 26×10^{-7} MN/m^2. The relation between the optical retardation and the principal stress difference could be discussed briefly as follows.

From the theory of photoelastic stress measurement (Dally and Riley 1965), the optical retardation, R, is proportional to the difference in the magnitude of

the principal stress. When the principal stresses are in a plane normal to the light path, R is given by

$$R = \frac{1}{f_\sigma} \int_{-\delta z}^{\delta z} (\sigma_{\theta\theta} - \sigma_{rr}) dz \qquad \text{1-a}$$

$$\frac{R}{2\delta z} = \frac{1}{f_\sigma} (\bar{\sigma}_{\theta\theta} - \bar{\sigma}_{rr}) \qquad \text{1-b}$$

where the sample is viewed in a direction, z, normal to the diffusion direction, $\sigma_{\theta\theta}$ and σ_{rr} are the principal stresses, $\bar{\sigma}_{\theta\theta}$ and $\bar{\sigma}_{rr}$ are the stresses $\sigma_{\theta\theta}$ and σ_{rr} averaged along z, $2\delta z$ is the length of the light path and f_σ is the stress optical coefficient.

In a sample where $2\sqrt{Dt} \ll \Delta r$, where D is the diffusion coefficient, t is the time of exchange and Δr is the raduis of the sample, the radial stress σ_{rr} is given by

$$\sigma_{rr} \approx \frac{R_{r=0}}{2\Delta r} \cdot f_\sigma \qquad 2$$

This value is free from the effect of slicing and light path bending.

Effect of the Compressive Stress
on
the Fracture of the Glass

McClintock and Walsh (1962) suggested that cracks subjected to uniform compressive stresses will close when a closure compressive stress, σ_c, is reached and the experiments of Hook and Bieniawski (1965) support this view. However, the situation for a crack on an exchanged glass surface, where the compression layer progressively advances from the open end of the crack is somewhat different. When a very small layer depth Δ, has been exchanged, it may be presumed that the force is too small to close the crack (even though the compressive stress may be higher than σ_c), these crack faces are expected to bend towards each other, Fig. 1-b. (Δ_c in Fig. 1 is the exchange depth at which the crack becomes closed, *i.e.* the

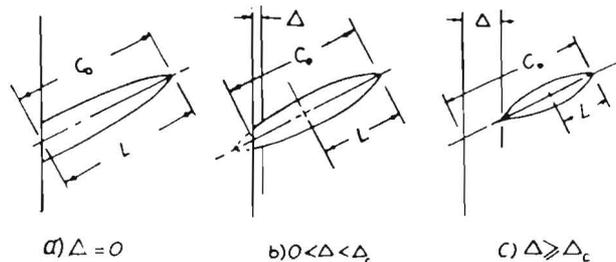a) $\Delta = 0$ b) $0 < \Delta < \Delta_c$ c) $\Delta \geqslant \Delta_c$

Fig. 1. Crack closure.

depth at which the open ends of the crack first touch). Fig. 1-a represents the crack before ion exchange, *i.e.* at $\Delta = 0$. Only after a certain finite depth has been exchanged does the force on the open end of the crack become sufficiently high to close the crack, Fig. 1-c. From this point on the McClintock postulate, a constant closure stress can be applied. For the case of $\Delta \ll (b-a)$ where b and a are the outside and inside radii of the glass tube respectively, the compressive stress, σ_c, is nearly independent of layer thickness Δ; and is constant throughout the exchange depth, while the tensile stress, σ_t, near the layer edge will be given by Abou-El-Leil and Cooper (1978).

$$\sigma_t = \frac{-b\sigma_c}{(b^2 - a^2)} \Delta \qquad\qquad 2'$$

Resolving the stresses in the direction of and normal to the crack axis yields the following normal compressive stress σ_{Nc} and shear stress T_c given by Abou-El-Leil (1978).

$$\sigma_{NC} = \frac{\sigma_c}{2} (1 + \cos 2\theta) \qquad\qquad 3\text{-a}$$

$$\tau_c = \frac{\sigma_c}{2} \sin 2\theta \qquad\qquad 3\text{-b}$$

Outside the layer, the normal and shear stresses σ_{Nt} and τ_t are given by

$$\sigma_{Nt} = \frac{\sigma_t}{2} (1 + \cos 2\theta) = \frac{-b\sigma_c}{2(b^2 - a^2)} \Delta(1 + \cos 2\theta) \qquad\qquad 4\text{-a}$$

$$\tau_t = \frac{\sigma t}{2} \sin 2\theta = \frac{-bc}{2(b^2 - a^2)} \sin 2\theta \qquad\qquad 4\text{-b}$$

(notice that moving from the compressive to the tensile zone rotates the principal stress direction by $\Pi/2$). The part of the crack inside the compressive layer Δ is expected to become closed Fig. 2-a.

The analysis can be simplified by considering the normal and sheer stresses separately as shown in Fig. 2b, 2c.

Experimental Technique

Specimens were cut from soda-lime glass tubes of inside radius 1.8 mm and outside radius 5 mm. The glass mol percentage composition was 67.7 SiO_2, 1.5 B_2O_3, 2.8 Al_2O_3, 0.6 k_2O, 15.8 Na_2O, 5.6 CaO, 4.0 MgO and 2.0 BaO, and its
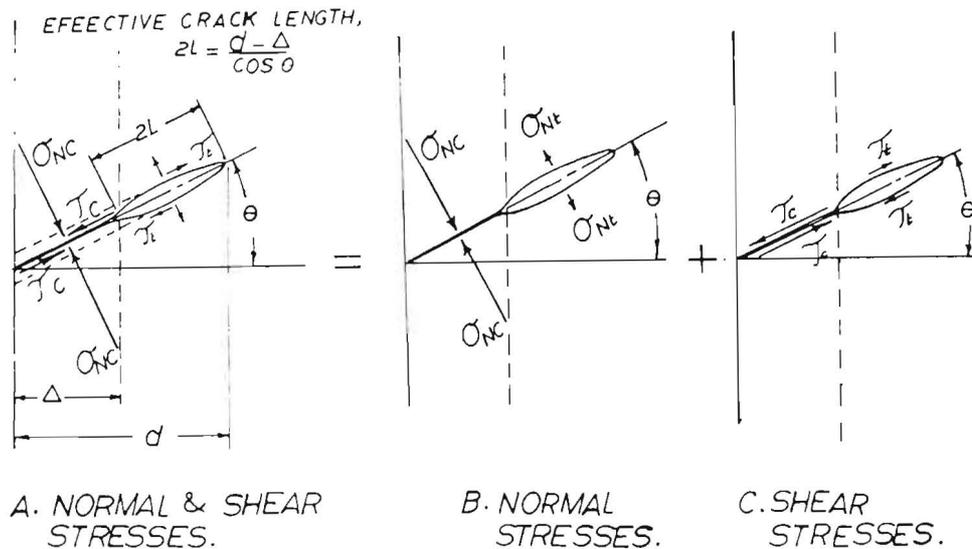
Fig. 2. Partial closure due to the stress.

stress optical coefficient was 26×10^{-7} MN/m^2 with a strain point of 486°C and an annealing point of 525°C. The field assisted ion exchange was carried out by applying a dc current of 200 mA for about 5 min at temperatures higher than 350°C to obtain exchange depth 12 μm. For temperatures lower than 350°C, the applied current was controlled according to both of the ion exchange temperature and the exchange depth. The tubes were exchanged in a molten bath of KNO$_3$ at higher temperatures and in 50% [KNO$_3$ + Ca (NO$_3$)$_2$] at lower temperatures. After field assisted ion exchange the samples were soaked in the molten salt of the potassium for different times and different temperatures. Stress measurements were carried out by reading a Berek compensator using a polarizing microscope.

Experimental Results

The results studied could be summarized under the following subheadings:

1. Exchange at Low Temperature Followed by High Temperature (Inwards) and at High Temperature Followed by Low Temperature (Inwards), (Single Ion Exchange)

Figure 3 shows the residual stress profiles for samples exchanged at two different temperatures 250°C and 450°C as marked on the figure. The results indicate that the value of the maximum stress difference at the edge of the exchange layer (see Fig. 2 and Fig. 3 given by Shaisha and Bahgat 1984) decreases from about
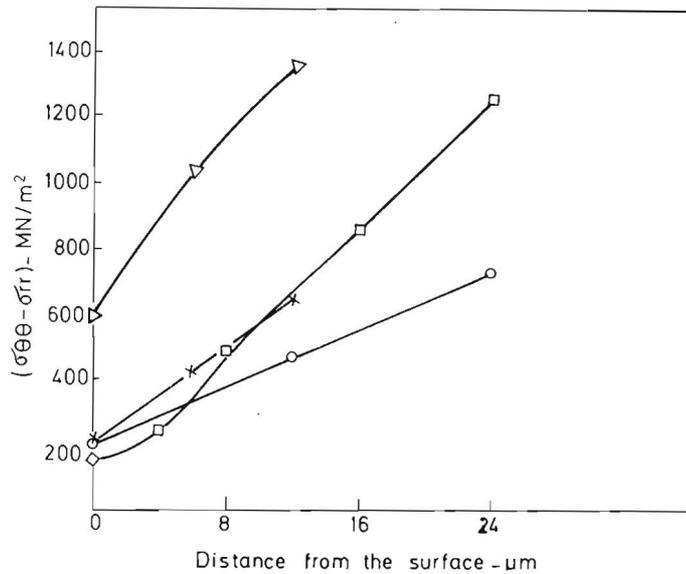
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Fig. 3. Single ion exchange at two different temperatures.
○ 250°C inwards then 450°C inwards.
□ 450°C inwards then 250°C inwards.
△ ion exchange at 250°C inwards.
x ion exchange at 450°C inwards.

1400 N/m^2 (ion exchange at 250°C) to about 750 N/m^2 when the sample was soaked at 450°C after ion exchange at 250°C. On the other hand, the value of the stress at the edge increases from about 650 N/m^2 (ion exchange at 450°C only) to about 1250 N/m^2 when the sample was soaked at 250°C after ion exchange at 450°C.

2. Exchange at Low Temperature Inwards Followed by Exchange at High Temperature Outwards and Vice Versa

The results obtained after ion exchange at 500°C inwards followed by ion exchanged at 300°C outwards, at 300°C inwards followed by ion exchange at 500°C outwards, at 300°C in both directions and at 500°C in both directions are presented in Fig. 4. These results display the following features:

a. The compressive stress in the exchanged double layer obtained by ion-exchange at high temperature (500°C) followed by ion exchange at low temperature (300°C) is higher than that obtained by the opposite process.

b. The stress resulting from the exchange at low temperature (300°C) is higher than that obtained in the other processes.

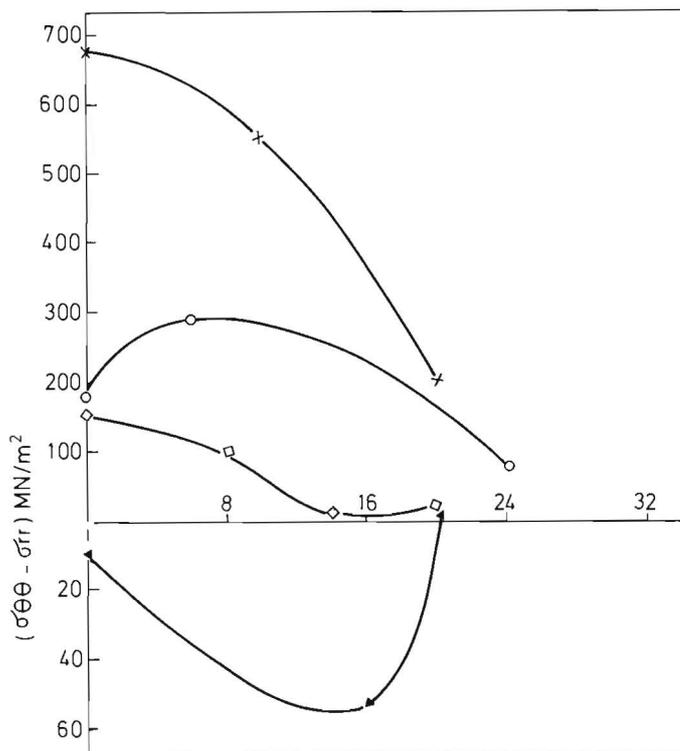c. A tensile stress arises due to the exchange at 500°C in both directions.

Fig. 4. Effect of reverse field at different temperatures.
x   300°C inwards then 300°C outwards.
○   500°C inwards then 300°C outwards.
□   300°C inwards then 500°C outwards.
△   500°C inwards then 500°C outwards.

3. Effect of Soaking at 350°C for Different Intervals of Time

The results of this section were studied for a glass tube which was ion ex-
changed at 350°C. A slice was taken out for stress measurements before soaking.
The rest part of the tube was soaked at 350°C for about 50 min and a slice was
taken out. The experiment was continued for different times at the same temper-
ature as indicated in Fig. 5. The results exhibit a decrease in the maximum com-
pressive stress with the increase of the soaking time. A rapid decrease in the stress
to about 50% of its value is obtained within a short time (12 hr). On the other
hand, the stress decreases from 400 to 220 MN/m^2 after a longer time (178 hr) as
shown in Fig. 6. The position of the maximum stress shifts towards the interior
with the increase of the soaking time and the depth of the compressive layer
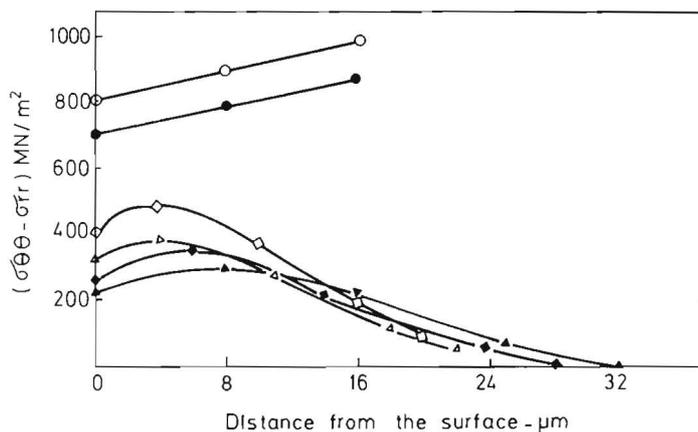increases with the soaking time.

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Fig. 5. Effect of soaking time after ion exchange at 350°C.
    ○   Without soaking.
    ●   Time of soaking 50 min.
    □   Time of soaking 12 hr.
    △   Time of soaking 30 hr.
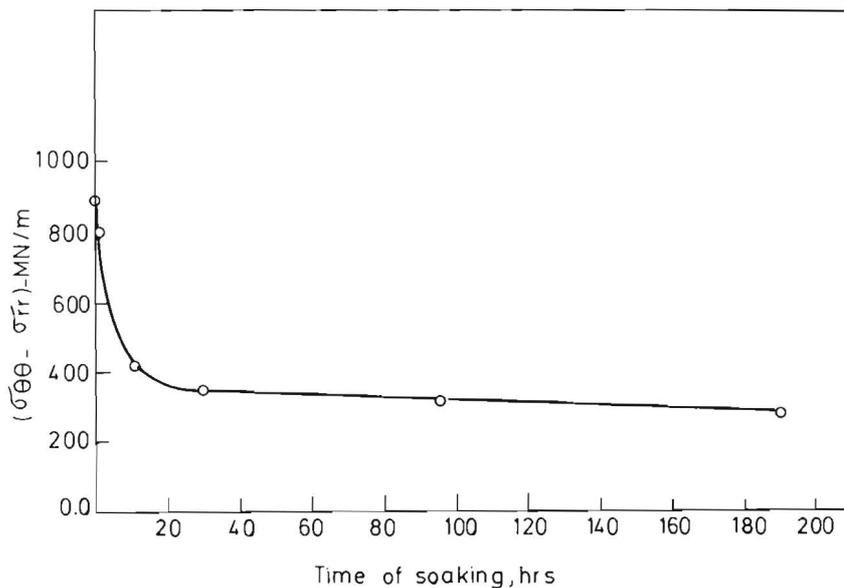   ■   Time of soaking 96 hr.
    ▲   Time of soaking 190 hr.

Fig. 6.   Residual stress against time of soaking at exchange depth 8 μm from the surface.

4. Effect of Soaking at Different Temperatures but Constant Time (20 hr)

Figure 7 shows the results obtained for a sample which was ion exchanged at 250°C and then soaked at 250 and 450°C for 20 hr. A stress relaxation was obtained after soaking at both temperatures 250 and 450°C. A tensile stress was revealed with maximum value at the exchanged layer surface after soaking at 450°C for 20 hr. At an exchange depth about 12 μm, the stress changed it sign, and a compressive stress was obtained with a maximum of about 100 MN/m^2.
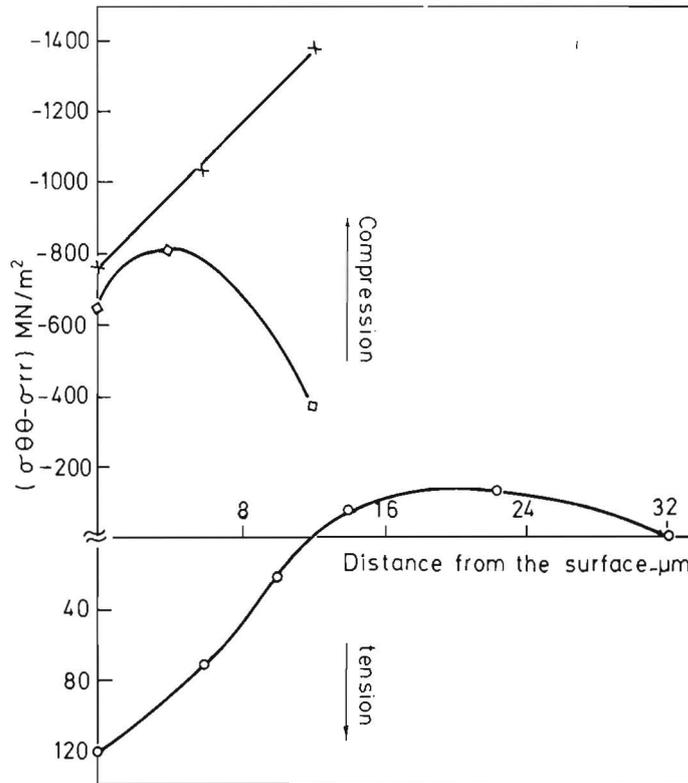

Fig. 7. Effect of the soaking temperature at constant time of 20 hr.
x   without soaking.
□   soaking temperature is 250°C.
O   soaking temperature is 450°C.

5. *Effect of Soaking at Constant Temperature of 300°C and Constant Duration of
   20 hr on the Stress Profiles of Samples Which Were Ion Exchanged at Different
   Temperatures*

Figure 8 shows a group of stress profiles for samples which were ion exchanged
at 250, 400 and 500°C before and after soaking at 300°C for a constant time of 20
hr. Comparing the values of the maximum stress at each ion exchange temperature
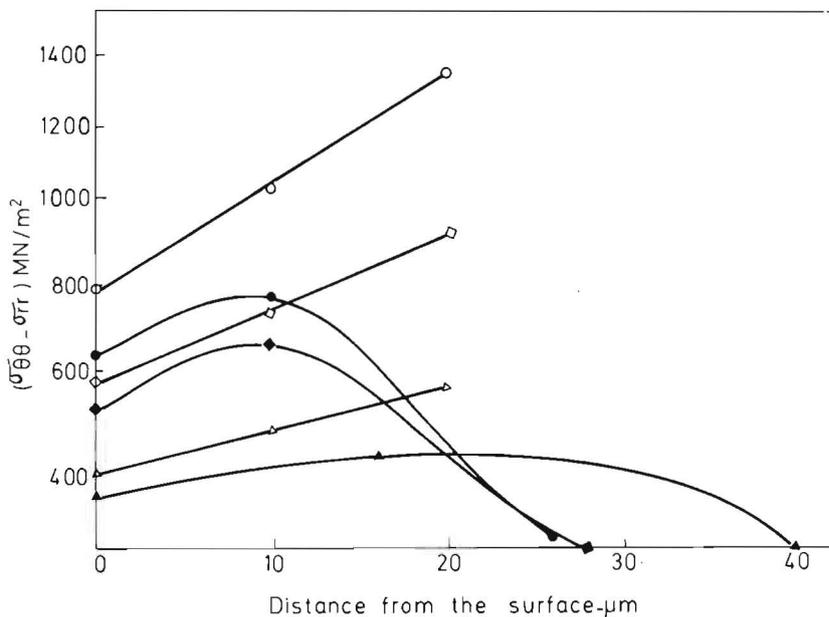before and after soaking, they were reduced to about 50% due to the soaking.

Fig. 8.   Effect of soaking at a constant temperature of 300°C and constant time of 20 hr.
   O   ion exchange temperature is 250°C (without soaking).
   ●   ion exchange temperature is 250°C (soaked at 300°C for 20 hr).
   □   ion exchange temperature is 400°C (without soaking).
   ■   ion exchange temperature is 400°C (soaked at 300°C for 20 hr).
   △   ion exchange temperature is 500°C (without soaking).
   ▲   ion exchange temperature is 500°C (soaked at 300°C for 20 hr).

Discussion

The results obtained can be discussed in terms of the relaxation mechanism
resulting from shear viscous flow and diffusional considerations. Since the strain
point of the soda-lime glass studied is 470°C, the effect of relaxation owing to flow
plays an important part for the compressive stress obtained by ion exchange at
high temperature. This type of relaxation has a great influence on the system of

stress profiles shown in Fig. 3 and 4. The results obtained in these two figures show that the stress relaxation depends on the final ion exchange temperature either in the single or double ion exchange. The stress is more relaxed if the final ion exchange temperature is high (450-500°C) even when the initial temperature is low (250°C). The value of the maximum compressive stress dropped from about 1400 MN/m^2 at 250°C to about 700 MN/m^2 when the glass was exchanged again at 450°C. As reported before by Shaisha and Cooper (1981) either the stress is a decreasing function of temperature or that there is a very fast stress relaxation process which occurs with a time constant which is much faster than the time of exchange.

The stress profiles obtained from a field assisted ion exchange followed by an ordinary diffusion ion exchange have a similar behaviour as that obtained by ordinary ion exchange only (Sane 1979). The results indicate a strong dependence on the soaking time, soaking temperature and the ion exchange temperature. A faster relaxation was obtained whenever any of these parameters increased. The dependence of the relaxation process on the soaking time and soaking temperature is governed by the relaxation time constant τ and a constance, b, which vary continuously with t/τ. The details of the theoretical analysis of this relation was treated by Sane (1979). In the following, a brief discussion concerning this relation is given.

The relaxation time constant τ is a function of b, as well as of temperature. For a fixed value of, b, e.g., b = 0.25, the expression for τ expressed in seconds can be written $\tau = 5.63 \times 10^{-15}$ (60.4 $\times$ 10^3/RT) seconds, for glass rods. It is possible to relate the time constant to a physical property of the glass. The parameter b, in the relaxation modulus, increases slowly with temperature. This parameter governs the distribution of the relaxation time constants. If the value of b is lower than 0.5, say b = 0.25, then it gives a much broader distribution so that the relaxation is rapid at small times (t $\ll \tau$) and slow at long time (t $\gg \tau$). Figure 6 demonstrates this effect. The measured stress profiles in ion exchanged samples provide ample evidence that the relaxation constants are widely separated, i.e. b is small. Such behaviour is observed even at high temperatures.

A faster relaxation than the predicted one near the surface could arise from a concentration dependence of τ. Such dependence could arise from the mixed alkali effect. The mixed alkali effect is such that the viscosity in mixed alkali glass is reduced by an order of magnitude. Such a variation in the relaxation time constant introduces coupling between the relaxation at different points in the glass. This coupling occurs due to the condition that the equilibrium of forces must be maintained at any instant.

A tensile stress was obtained at high temperature (500°C which is above the strain point) either in double exchange layer (Fig. 4) or after soaking for long time (Fig. 7). These results agree with those obtained by Shaisha and Cooper (1981). By analogy to the thermal tempering, at high temperature the stress is relaxed viscoelastically resulting in a nearly stress-free state with a nonuniform temperature

distribution. The differential changes in length between this state and the isothermal state at room temperature must be accommodated elastically and the stress state is reversed producing a tensile stress.

Conclusion

The residual stress relaxation in a field assisted ion exchanged glass is greatly effective by soaking the ion exchanged glass samples at the molten salt of potassium nitrate for different temperatures and different times. The stress relaxation was observed even the soaking had been carried out at low temperature (250°C). The stress relaxation is increasing as the soaking temperature and soaking time increase. Both of these two parameters are governed by the relaxation time constant τ. The stress relaxation near the surface of the compressive layer could be due to the concentration dependence of the relaxation time constant.

The lower stress in the doubly exchanged layer compared to that in the singly exchanged one is not due to the lower potassium content in the double exchanged layer alone but also due to some relaxation mechanism.

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استرخاء الإجهاد الناتج من التبادل الأيونى فى الزجاج

*البيلى إسماعيل شعيشع و علاء الدين عبد الحميد بهجت

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لقد تم غمس مجموعة من أنابيب زجاج سيليكات الصوديوم التى حدث فيها تبادل أيونى باستخدام المجال الكهربى فى محلول أيونى من نترات البوتاسيوم عند درجات حرارة مختلفة وفى فترات زمنية مختلفة .

تمت دراسة تأثير كل من عامل درجة الحرارة والزمن على قيم الإجهاد المتبقى فى الزجاج، كذلك تمت دراسة الإجهاد المتبقى الناتج من التبادل الأيونى عند تطبيق المجال الكهربى فى اتجاه واحد وفى اتجاهين متضادين ومناقشة تأثير عكس اتجاه المجال الكهربى على الاسترخاء فى الإجهاد المتبقى . وتم بعد ذلك مناقشة النتائج بدلالة استرخاء الإجهاد والانتشار الأيونى .