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LETTER

Estimation of ion exchange layers for soda-lime-silicate glass from curvature measurements

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Many commercial glasses exhibit subcritical crack growth in the presence of environments that contain water. The phenomenon of subcritical crack growth is strongly dependent on the pH of the environment (see e.g. Wiederhorn and Johnson [1], Simmons and Freiman [2] and Gehrke et al. [3–5]). Both the shape and position of the crack growth curve can change as a function of pH—static fatigue limits can be created or can disappear [3–5], as can low stress intensity factor, crack-growth plateaus [2, 5]. Often the pH at the crack interface is determined by the composition of the glass itself [6], as the process of ion exchange between mobile alkali ions in the glass and hydronium ions in the water leaves behind an excess of hydroxyl ions and consequently a basic solution at the crack interface. Furthermore, glasses like silica glass, which have no mobile ions, have acidic solutions [6], because of the acidic nature of the silanol groups that cover the fracture surface of the silica glass in water.

In addition to controlling the pH of the interface solution, the ion exchange process results in surface stresses that lead to a static fatigue threshold in the glass, or to low level crack growth plateaus [7, 8], depending on the sign of the stress. The interdiffusion of either hydrogen ions (H^+) or hydronium ions (H_3O^+) with the Na^+ ions in the glass is the main cause of stress development within the ion exchange layer. These stresses influence the stresses near the crack tip, inducing either a positive or negative change in stress intensity factor, again depending on the sign of the ion exchange stress. H^+/Na^+ exchange results in a tensile stress in the hydration layer because the H^+ ions are smaller than the Na^+ ions they replace. The tensile stress in the hydration layer in turn results in an increase in the stress intensity factor. By contrast, the H_3O^+/Na^+ exchange leads to a compressive stress in the fracture surface and a reduction of the crack tip stress intensity factor.

Measurement of the hydrogen and soda profiles [9] revealed a ratio between the hydrogen concentration in the surface of the hydrated glass and the sodium concentration in the unhydrated glass of 2.9 ± 0.3. This three-to-one replacement of Na^+ by H^+ suggests that Na^+ is replaced by H_3O^+ and that the stress in the surface exchange layer is compressive. As suggested by Michalske and Bunker [7], this compressive stress is a cause of a static fatigue threshold in glasses that contain mobile sodium cations.

To study the effect of exchange layers on crack growth, Michalske and Bunker [7] measured the mechanical response of glass disks to ion exchange after contact with water at one of the surfaces. For this purpose, they metalized the glass disk on its upper surface and sealed it into the end of a tube. The free surface of the glass disk was then exposed to different aqueous solutions. By use of an optical interferometer, the curvature of the disk could be monitored, from which stresses and strains in the ion exchange layer were estimated. From measurements carried out on sodium borosilicate glass with a composition of 30% Na_2O, 10% B_2O_3 and 60% SiO_2 by molecular weight, Michalske and Bunker [7, 8] demonstrated the presence of tensile stresses within the ion exchange layer for glasses immersed in solutions of 0.5 M HCl and 5 M HCl. For a second glass with a composition of 10% Na_2O, 10% B_2O_3

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and 80% SiO_2, by molecular weight, no measurable curvature was found. These authors used a fracture mechanics formalism (originally developed to determine the fracture toughness of ZrO_2 [10]) to approximate the stress intensity factor caused by the development of ion-exchange layers at the free surfaces of cracks in glasses. They demonstrated how surface stresses may affect crack growth in glass, either enhancing or retarding crack growth depending on the stress.

In order to understand the effects of the environment on the threshold stress intensity factor, it is necessary to understand the influence of pH on the development of ion exchange layers, especially the sign of volume change in those layers. Therefore, the aim of the present investigation is to determine the sign of the volumetric strains in the ion exchange layers for two commercial soda-lime-silicate glasses as a function of the pH of the liquid environment.

The compositions of the glasses studied are given in Table 1. Material (I) is a commercial soda-lime-silicate glass with a high content of alkaline earth oxides (AR glass, Schott GmbH, Mainz). Material (II) was used in an earlier series of studies of crack growth in soda-lime-silicate glass. The composition was reported in reference 1; the composition in Table 1 is from a more recent analysis [11]. The composition is almost identical to that reported earlier. Soda lime glass (III) was used by Lanford et al. [9] for a study of H_3O^+/Na^+ ion exchange.

Before testing, any ion exchange layers introduced during the polishing procedure had to be removed. We therefore applied a surface treatment as recommended by Pantano (personal communication). According to this suggestion, the slides were first annealed at 520 °C, then etched in 1 M NaOH at 80 °C for 10–20 min and finally rinsed in 1 M HCl at room temperature, followed by rinsing in water. Annealing of the slides reduced global residual stresses in the slides, while, the etching procedure removed pre-existing ion exchange layers.

The experimental setup to measure surface curvature resulting from ion exchange is shown in Fig. 1. Glass microscope slides $75 \times 25 \times 1\ \text{mm}^3$ in dimension for material I and $75 \times 25 \times 1.5\ \text{mm}^3$ for material II were positioned on three needle-like supporting points. The LVDT measured the displacement in the centre of the glass slide (A) against the three pin points (B). The set-up on three points each ensures statically well-defined support conditions. The liquid in the basin comes in contact with the glass only at the lower surface. This leads to a curvature of the slide if a volume change in the ion exchange layer occurs.

Bending strains averaged over 28 single tests (for each curve number given in brackets) are shown in Fig. 2a for composition (I) as a function of time. The pH value of pH = 13 was obtained by 0.1 M NaOH concentration, the value pH = 1 by 0.1 M HCl concentration and a nominal pH = 7 was approximated by using distilled water[1].

In Fig. 2b, the strains at $t = 300$ min are plotted versus pH. Positive strains were found in the range of $1 \le \text{pH} \le 13$. The individual results are indicated by the small symbols, the mean values by the larger ones. The perpendicular lines represent the region of 2 standard deviations (SD). Figure 3 represents results obtained for glass composition (II).

The sample thickness was measured before and after the test with an accuracy of ±0.02 mm. Thickness changes during the tests were not detected. This is not astonishing since ion exchange layer thicknesses are of the order of a few nanometers maximum (see e.g. [9]). From the density changes in these zones, thickness changes of less than a nanometer have to be expected.

From the measured displacement, δ, the bending strain is obtained from Eq. 1:

$$\varepsilon_{\text{bend}} = \frac{4W}{L^2}\,\delta \tag{1}$$

From the bending strain $\varepsilon_{\text{bend}}$, the volumetric strains ε_{vol} in the ion exchange layers can be determined. According to the Bernoulli hypothesis (plane cross-sections remain plane after deformation), the strain distribution through the thickness is linear (see Fig. 4).

Since stresses and strains are biaxial, $\sigma_x = \sigma_y$ and $\varepsilon_y = \varepsilon_x$, it holds

$$\varepsilon_x = \varepsilon_y = A + Bz = \begin{cases} \frac{\sigma_x}{E}(1-\nu) & \text{for}\, z > -(W/2-b) \\ \frac{\sigma_x}{E}(1-\nu) + \varepsilon_0 & \text{for}\, z \le -(W/2-b) \end{cases} \tag{2}$$

where ε_0 is the linear strain in the layer of thickness b and ν is Poisson's ratio.

The bending strain measured by the LVDT is exclusively given by the coefficient B as

$$\varepsilon_{\text{bend}} = \frac{1}{2} BW = 3\,\frac{\varepsilon_0 b}{W} \tag{3}$$

In order to determine the unknown B, let us multiply Eq. (2) by z and integrate over the thickness W

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[1] We took no account of the carbon dioxide dissolved in the water. For such a weak acid, the pH may have been controlled by interaction with the glass surface. We did not measure the pH of the solutions after they were made or used.

Table 1 Compositions of soda-lime-silicate glasses (in weight percent)

Material	SiO_2	Na_2O	CaO	Al_2O_3	MgO	K_2O	BaO	B_2O_3
I	69%	13%	5%	4%	3%	3%	2%	1%
II	74%	14%	5.9%	1.8%	3.7%	0.36%		
III	72%	15.9%	7.9%	1.4%	2.4%	0.1		

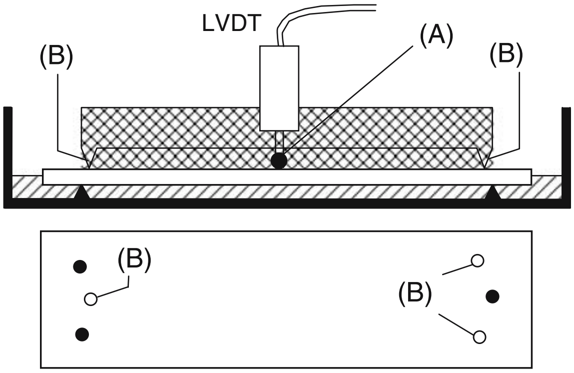

Fig. 1 Inductive test device (solid circles: supporting pin points, open circles: pin points of the measuring system)

$$\int_{-W/2}^{W/2} \varepsilon_x z\,\mathrm{d}z = 112BW^3 = \underbrace{\frac{1-\nu}{E}\int_{-W/2}^{W/2} \sigma_x z\,\mathrm{d}z}_{\substack{=0,\\ \text{dis appearing}\\ \text{total moment}}} + \int_{-W/2}^{-(W/2-b)} \varepsilon_0 z\,\mathrm{d}z \Rightarrow B = -6\varepsilon_0 b/W^2 \tag{4}$$

in agreement with Stoney's equation [12]. Having in mind that the volumetric strain $\varepsilon_{\mathrm{vol}}$ is 3 times the linear strain ε_0, it finally holds that

$$\varepsilon_{\mathrm{bend}} \cong \frac{\varepsilon_{\mathrm{vol}} b}{W} \tag{5}$$

Relation (5) allows one to determine the product of volumetric strain $\varepsilon_{\mathrm{vol}}$ and layer thickness b from the measured bending strain.

Figure 5a shows the mean values and spans of two standard deviations for the product of the layer thickness b and the volumetric strain $\varepsilon_{\mathrm{vol}}$ after 5 h for glasses (I) and (II), as obtained by Eq. (5). In the case of expansive strains, we assume a replacement of Na^+ by H_3O^+, which results in a positive volume change of about $\varepsilon_{\mathrm{vol}} \cong 7.1\%$ for glass (I) and 6.6% for glass (II) (for the determination of these values from the composition see [11]). In the case of glass I in distilled water, $b \approx 6.5$ nm at pH = 7. For glass (II) b = 14 nm at pH = 7 and 7.8 nm at pH = 13.

Figure 5b shows measurements of the ion exchange layer thickness b of a soda lime glass (material III in Table 1) in pure water for a temperature range of ≅70–90 °C as reported by Lanford et al. [9]. The layer thickness was found to be proportional to the square-root of time and to have an Arrhenius dependence on temperature [9]:

$$b = C\sqrt{t}\exp(-Q/RT) \tag{6}$$

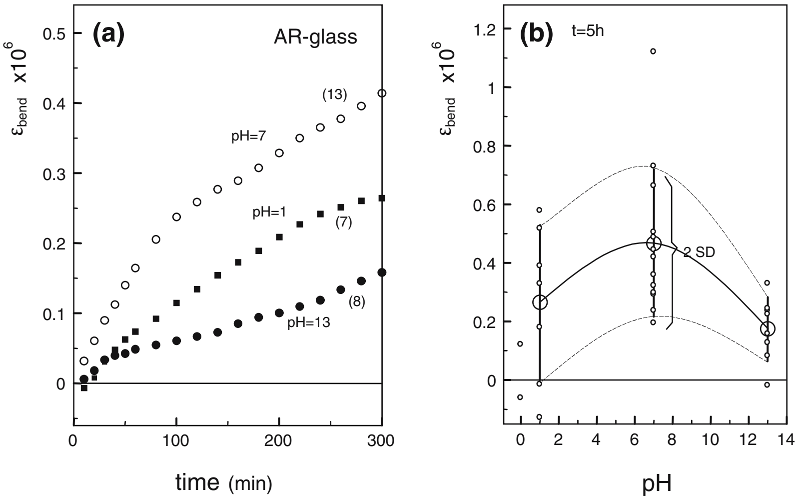

Fig. 2 Results for glass composition (I), (**a**) influence of time for tests in different environments (average over a number of single tests; number of tests in brackets), (**b**) effect of pH for t = 5 h

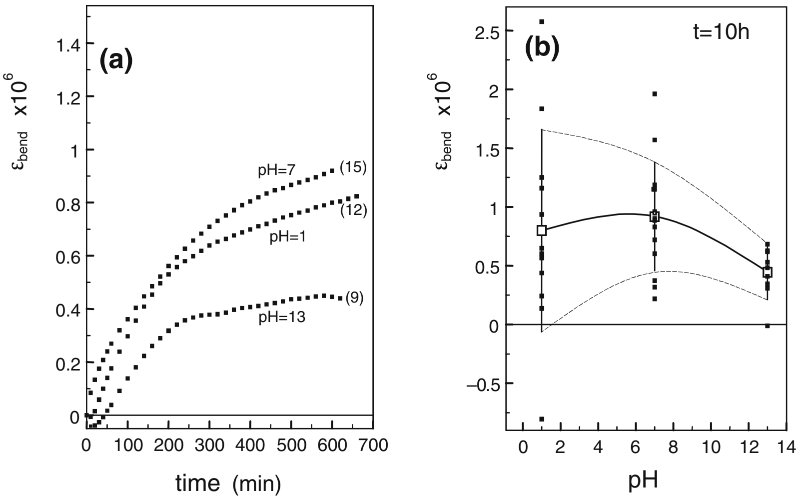

Fig. 3 Results for glass composition (II), (**a**) influence of time for tests in different environments (average over a number of single tests; number of tests in brackets), (**b**) effect of pH

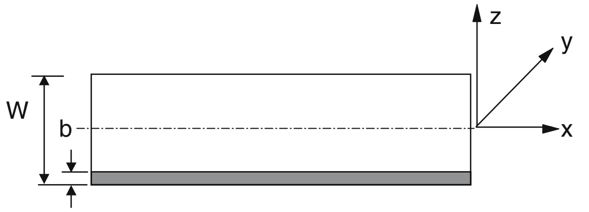

Fig. 4 Cross section through the plate thickness (geometric data)

with $C = 0.00938$ m/√h and an activation energy Q = 38.6 kJ/mol ($R = 8.31$ J/mol k). From this relation we obtain $b = 3.2$ nm for $t = 5$ h.

Thus, the layer thickness estimated from our studies, Fig. 5a is a factor of from 2 to 5 times smaller than the values estimated from the Lanford studies, Fig. 5b. This difference in results may be the consequence of the slight differences in compositions shown in Table 1. To have avoided this possibility, it would have been best to carry out our studies simultaneously with the Lanford studies and on exactly the same glass as used by Lanford et al. [9]

Possible explanations for the results could be differences in diffusion rate as a consequence of small differences in glass composition. We saw substantial differences in strain between glasses I and II as a consequence of small differences in chemical composition. Perhaps small differences in composition between II and III will also account for the difference in a factor of two between results obtained on these two glasses. Alternatively, our estimate of the volume change due to ion exchange may be too large. A decrease in our estimate of the volume change by a factor of two would bring glass II and glass III into coincidence. Finally, decomposition of hydronium ion into a proton and water after penetration into the glass, with the water migrating out of the glass, could easily explain an error in the estimated volume change. Lanford et al. [9]

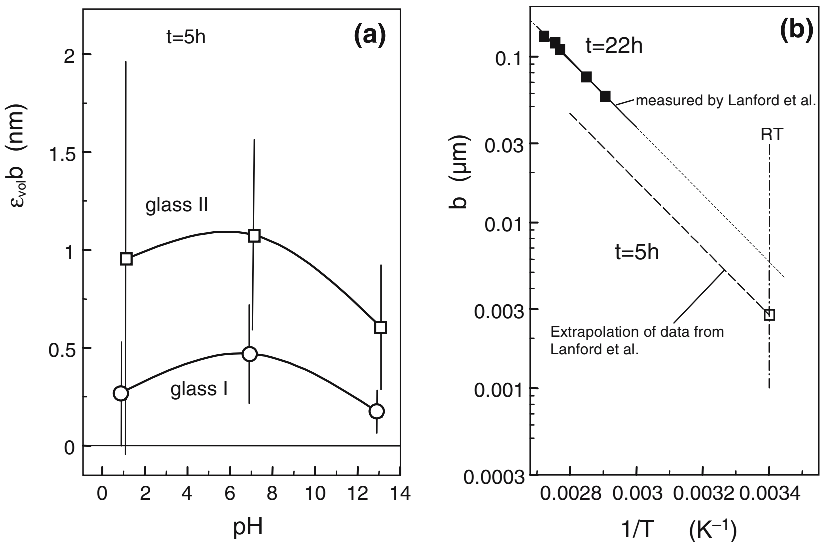

Fig. 5 Product of volumetric strain and layer thickness, (**a**) glasses (I) and (II), (**b**) extrapolation of measurements for glass (III) [9] to $t = 5$ h and room temperature

noted this possibility in his study; to slow down the water migration, he kept his specimens in cold storage until they were analysed.

Whatever the case, we are encouraged by the fact that the bending was a consequence of a compressive force in the surface of the ion exchange sample. This result is consistent with the exchange of hydronium ions in the crack-tip solution with sodium ions in the glass. Further quantification of these results will require additional experimentation

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