Journal of Non-Crystalline Solids 427 (2015) 91–97

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Buildup and relaxation of stress in chemically strengthened glass

Arun K. Varshneya [a,b,*], Garrett A. Olson [a], Patrick K. Kreski [a,b], Prabhat K. Gupta [a,c]

[a] Saxon Glass Technologies, Inc., Alfred NY 14802
[b] Alfred University, Alfred NY
[c] Ohio State University, Columbus OH

ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form 16 July 2015
Accepted 17 July 2015
Available online 25 July 2015

Keywords:
Glass;
Ion exchange;
Molecular dynamic simulation;
Stress birefringence;
Stress buildup;
Structural relaxation

ABSTRACT

Cooper–Krohn analysis of stress generation in soda lime silicate ("SLS") glasses during ion exchange strengthening suggests that the glass should develop 2.5 to 3 GPa surface compression (biaxial stress), though only ~600 MPa values are observed experimentally. In this paper, we suggest that this "network dilation anomaly" is largely resolved. MD simulations were carried out to monitor volume and pressure changes after ion-swap. Surface compression in an SLS glass ion-exchanged as a function of temperature and time in KNO_3 bath was measured to follow the viscous relaxation. We show that biaxial surface compression builds initially to the expected ~2.5 GPa; thereafter fast secondary structural ("β") relaxations, whose time constants span picoseconds to nanoseconds, cause the surface compression to relax rapidly to ~1.5 GPa at the ion exchange temperature. Stress relaxes thereafter due to "α" primary structural relaxations associated with viscous flow. Recovery occurs to a transition state which is somewhat short of the expected glass volume. Full volume is recovered at higher temperatures due to increased flow.

1. Introduction

Since the discovery of the glass chemical strengthening process in the early 1960s, the single most important commercial application has been the aircraft cockpit windshields which constitute two or three layers of glass laminated with polyvinyl butyrates or polyurethane to withstand bird hits at speeds of 400 knots per hour. The primary advantage of the chemical strengthening process over the traditional thermal tempering process is the development of high surface compression, of the order of 600 MPa, which helps increase the windshield modulus of rupture immensely. In recent years, the use of scratch-resistant strengthened thin cover glasses in personal mobile electronic devices such as cell phones and electronic tablets has renewed interest in the chemical strengthening process. Other applications such as chemically strengthened glass cartridges for autoinjectors as an emergency antidote to avoid anaphylactic shock in severe cases of allergies to bee stings, peanuts and shellfish have also drawn attention because of their importance in lifesaving situations. Benefits and drawbacks of the chemical strengthening process relative to the thermal tempering process can be found elsewhere [1].

The development of surface compression in metals using nitridation was described by analogy to thermal stresses by Richmond et al. [2]. This formalism was then adopted to describe ion exchange strengthening in alkali-containing glass by Cooper and Krohn [3]. For a semi-infinite sodium-containing glass sheet of thickness $2L$ which is exchanged symmetrically in the x-direction (thickness direction) by immersing in a molten salt such as KNO_3, the stresses at location x are given by [1]:

$$[\sigma_{yy}]_x = [\sigma_{zz}]_x = -BEC/(1-\nu) + [BE/2L(1-\nu)]\int_0^{2L} C dx \qquad (1)$$
$$\text{and } [\sigma_{xx}]_x = 0,$$

where E = Young's modulus, ν = Poisson's ratio, and B = linear network dilation coefficient "LNDC"

$$= 1/3[\partial \ln V/\partial C] \qquad (2)$$

The first term represents a compression due to stuffing from the local concentration of the invading ion and the second term represents a balancing tension due to elastic compatibility. Cooper also proposed that an unconstrained K-exchanged glass will have a molar volume V_{mK} which corresponds to that of the compositionally equivalent as-melted ("CEAM") glass. Hence, the LNDC should be given by

$$B = [1/3C_o]\,\mathrm{Ln}(V_{mk}/V_{mNa}) \cong [V_{mk} - V_{mNa}]/3V_{mNa}C_o \qquad (3)$$

where V_{mNa} is the molar volume of the parent Na-containing glass and C_o is the mol% or mol fraction of alkali in glass that exchanges. The factor of 3 converts a volume coefficient to a linear coefficient.

The quantity BC_o represents the linear expansion of the glass network which is constrained by the unexchanged substrate from

---

* Corresponding author at: Saxon Glass Technologies, Inc., 200 N. Main Street, Alfred, NY 14802, United States.
E-mail address: varshneya@alfred.edu (A.K. Varshneya).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.07.037
0022-3093/

expanding to its CEAM value and is responsible for the generation of surface compression.

$$\left[\sigma_{yy}\right]_o = [\sigma_{zz}]_o \cong -BEC_o/(1-\nu) = -\,[E/(1-\nu)][V_{mK}-V_{mNa}]/3V_{mNa} \quad (4)$$

Stress measurements in a semi-infinite ion-exchanged plate glass specimen are often made using two techniques:

(1) using ellipsometry (or refractometry) on the flat face of the chemically strengthened x-plane nondestructively, and
(2) using optical birefringence through a thin slice containing the diffusion direction *x* (see ASTM C-1422, Ref [5]).

In the first experiment, one measures the biaxial stress $[\sigma_{yy}]_o$ which is the planar stress on the surface assuming plane-strain condition. In the second experiment, one measures $\sigma_y - \sigma_x$ which is exactly equal to $[\sigma_y]_o$ at the surface under a plane-stress assumption. From the measured $[\sigma_y]_o$, it is customary to report the "unbroken plate" stress which is essentially the biaxial stress $[\sigma_{yy}]_o$ by using the relationship $\sigma_y / (1 - \nu) = \sigma_{yy}$.

It has long been recognized [4] that values of *B* computed from measured molar volumes of the host glass and that of the CEAM glass are usually 3 to 5 times those computed from the experimentally measured stresses. The sizable discrepancy of surface compression developed during ion exchange between that measured and that expected from theory, otherwise called the "dilation anomaly", has remained controversial for nearly four decades.

Measured values of $[\sigma_y]_o$ or $[\sigma_{yy}]_o$ in chemically strengthened soda lime silicate glasses are usually only about 400 to 600 MPa — far lower than that calculated from as-melted molar volumes (~2 to 2.5 GPa). Sane and Cooper [6] were unable to relate the disparity to viscous flow during ion exchange. Garfinkel and King [7], Varshneya [8], and Glebov et al. [9] suggested that some initial network accommodation of the invading ion, a "plastic deformation", is responsible for reduced buildup of stress. In particular, Varshneya [10] suggested that plastic deformation effectively superimposed a reverse stress field which reduced the observed surface compression.

One other source of loss in the observed surface compression magnitude is due to the differential thermal contraction of surface layers upon cooling from the ion exchange temperature to ambient. Tyagi and Varshneya [11] have shown that the K-exchanged surface layers appear to have significantly higher thermal contraction coefficient relative to the substrate, accounting for a loss of ~20–25% in the magnitude of the surface compression. While this decrease reduces the disparity, the observed stress remains about 1/3rd that expected from as-melted molar volumes.

Laboratory measurements of stress in flat specimens do not yield useful information on stress buildup and relaxation for ion exchange times less than about 10 min, primarily because penetration of ions less than ~3 μm does not yield accurate stress measurements using any of the optical birefringence based techniques.

The use of molecular dynamic (MD) simulations elucidates some of the missing early time information, up to ~10^{-7} s, with one important caveat. At present, MD simulations have not been attempted for glass geometries used in laboratory ion exchange experiments (uniaxial interdiffusion). The best one can do is to conduct the simulation on a cube of homogenized material where a fraction of alkali ions (0 to 100%) are swapped homogeneously and equilibrated under either NVT (constant number, volume, and temperature) constraint or under NPT (constant number, pressure, and temperature) constraint. Under NVT conditions, the pressure buildup from the stuffing of large ions and its subsequent relaxation, if any, are monitored. During NPT conditions (usually at $P = 0$), the volume change is monitored with time.

MD simulations at NVT in a 3-d ensemble yield pressure *p* that generates after uniformly swapping ions. To compare the results of the MD simulation with those of ion exchange experiments involving thick plates having biaxial system of stresses, one needs to compute the equivalent plane-strain biaxial σ_{yy} (or thin slice plane stress σ_1) using the same strain generating mechanism. As shown in Appendix A, this is achieved for isotropic solids such as glass by recognizing

$$p = K\ \Delta V/V = E\ \Delta V/3(1-2\mathrm{v})\mathrm{V} \quad (5)$$

where *K* is the bulk modulus, and ΔV is the change in the volume. Hence, to obtain biaxial stress σ_{yy} equivalent of $-p$, we multiply $-p$ by $[(1 - 2\nu) / (1 - \nu)]$. Likewise, to obtain a thin slice equivalent stress σ_1, we multiply $-p$ by $(1 - 2\nu)$. [Henceforth, the negative sign for compression will be dropped].

In the laboratory, only a few microns of the surface are usually exchanged. Biaxial stress is generated as a consequence of the constraining substrate. If we assume that the substrate is much larger in thickness than the surface exchanged region, then the biaxial stress on the free surface in the laboratory experiment could be compared to the biaxial equivalent of the pressure generated in the swapped volume in MD simulations using the above relations. Likewise, reported thin slice stress measurements can be scaled appropriately.

The purpose of this paper is to take an inventory of the buildup of surface compression at "zero time" and to reconcile the measured stresses with volume changes and relaxation estimates. We have conducted MD simulations for $15Na_2O\cdot10CaO\cdot75SiO_2$ (mol%) glass beginning with the instant of swapping the Na^+ ions with K^+ ions. Whereas most simulations in the past have only been carried out at the most to 3 or 4 ns, we have carried these simulations out from picoseconds to as much as 60 ns segments under cascaded NPT, NVT and NPT constraints. Next, we have carried out laboratory chemical strengthening experiments in a commercial soda lime silicate glass to determine the stress relaxation data in an effort to obtain zero time surface compression by extrapolation. Finally, the MD early time information and the laboratory later time data are pieced together to follow stress buildup at $t = 0$ and the subsequent stress relaxation and associated volume changes.

2. MD simulations

MD simulations used 6000 atoms of composition $Na_{620}Ca_{207}Si_{1552}O_{3621}$ which is close to $15Na_2O\cdot10CaO\cdot75SiO_2$ (mol%) glass with cubic periodic boundary conditions. Details of the procedure are given by Kreski et al.[12]

After cooling from 6000 K, the structure was equilibrated at 723 K (typical ion exchange temperature) for 20 ns under NPT ensemble. Next, the system was equilibrated under NVT ensemble for 10 ns to ensure the pressure development in the subsequent ion swapping step was not an artifact of the change of ensemble. After NVT equilibration, all Na ions were relabeled as K ions while maintaining NVT constraint. Pressure was monitored for as much as 60 ns for the 723 K simulation. The early stage relaxation under NVT after swapping was sampled at fractions of picosecond intervals for improved resolution. The constraint was then changed over to NPT ($P = 0$) and the volume expansion was monitored for 20 ns. Separately, the K-swapped random ensemble was equilibrated at 6000 K in the usual way and equilibrated under NPT conditions at 723 K to yield the CEAM structure.

3. Experimental procedure

The nominal chemical composition of the soda lime silicate glass chosen for the laboratory portion of this study was $12Na_2O\cdot6MgO\cdot9CaO\cdot71SiO_2\cdot2(\mathrm{Others})$ in mol%. Its relevant physical properties were strain point 511 °C, annealing point 554 °C, density 2.5 g/cm^3 and stress optic coefficient 2.76 TPa^{-1}. Specimens, 25 mm × 25 mm × 0.4 mm thick were obtained from a commercial supplier. These specimens were ion exchanged in a bath of technical