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Degradation of ion-exchange strengthened glasses due to surface stress relaxation

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ABSTRACT

Ion-exchange is a popular method to strengthen alkali-containing glasses. However, the experimentally observed residual compressive stress profiles often deviate from the theoretical profiles: a subsurface compression maximum is often observed, while monotonically decreasing stress with depth is expected. It is suggested here that this discrepancy can be accounted for by considering a surface stress relaxation process that takes place at a faster rate than bulk stress relaxation in the presence of water. This suggestion is based upon experimental data indicating the presence of water impurity in the molten salt used for ion-exchange strengthening of glasses. Recent work characterizing surface stress relaxation in oxide glass fibers as a diffusion controlled process aided by molecular water diffusion was applied to better explain the development of a subsurface compressive maximum within an accelerated timeframe. By combining the new surface stress relaxation diffusion mechanism with the well-established ion-exchange mechanism, a mathematical model predicting a subsurface maximum stress is developed with a good agreement to published data.

1. Introduction

Strengthening of alkali-containing glasses can be accomplished by using ion-exchange processing [1]. The method involves heat-treating alkali-containing glasses below the glass transition temperature in a molten salt bath containing larger alkali ions than those present in the glass. Inter-diffusion between the larger salt bath ions and smaller glass surface ions results in the glass acquiring a surface compressive stress and consequently an increase in mechanical strength. General features of the surface compressive stress profile can be calculated from the concentration profile of inward diffusing alkali species [2]. However, there are some discrepancies between the theory and experimental data [3,4]. One of these discrepancies is the presence of a subsurface compression maximum, shown in Fig. 1 for an ion-exchanged soda-lime silicate glass, taken from a paper by Sane and Cooper [5]. The main feature of this compressive stress peak is that with an increasing treatment time it moves to greater depths while reducing in magnitude.

Sane and Cooper [5] attempted to model the observed behavior using bulk stress relaxation introduced by a stretched exponential function. They concluded, however, that the expression was unable to capture the observed experimental behavior regardless of the stretching exponent used. In fact, Sane and Cooper's equation can produce a subsurface peak, but on a time scale much greater than those observed experimentally. These observations indicate that the surface region was not being appropriately treated.

Various other theories have been proposed to explain the subsurface compressive stress maximum [6–10]. These theories include concepts such as composition-dependent material properties in the ion-exchanged surface region, densification of glass during ion-exchange, and viscoelastic relaxation. In spite of these numerous theories, the origin of a subsurface compressive stress maximum that develops within a very short timeframe remains unexplained. It is the purpose of the present work to explain this anomalous feature using a diffusion-controlled surface stress relaxation mechanism. The surface stress relaxation mechanism is known to take place at a much faster rate than bulk stress relaxation in the presence of water or water vapor [11,12].

In Section 2 it will be shown that molten KNO_3, commonly used for ion-exchange processing, contains water impurities, and that these water impurities can promote surface stress relaxation during the ion-exchange strengthening process. The value of the surface stress relaxation diffusion coefficient of soda-lime silicate glasses during the ion-exchange strengthening process will also be estimated.

In Section 3, the simulation of surface stress relaxation of glasses concurrent with ion-exchange strengthening is conducted to show that the time-dependent development of the subsurface compression maximum of ion-exchanged glass can be more closely modeled. Two different models will be presented which incorporate surface stress relaxation by modifying the bulk stress relaxation time, τ. The first model will treat the surface region within a sharp front of diffusing bond

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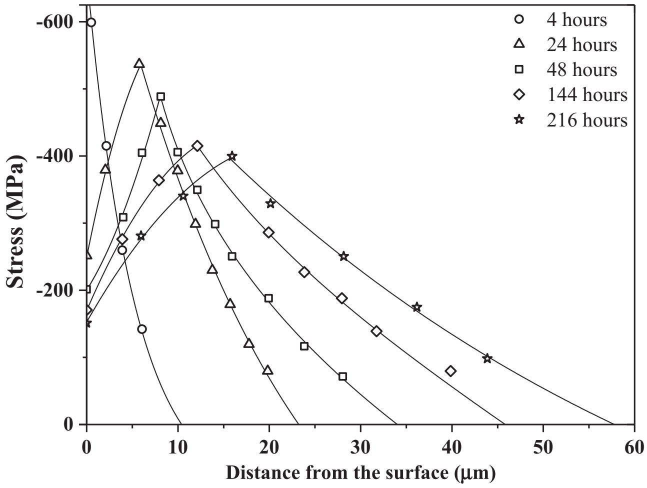

Fig. 1. Compressive stress profiles measured at 400 °C at various ion exchange treatment times for soda-lime silicate glass. Note that the compressive stress maximum is not at the surface or location of highest ion concentration, but rather at some depth into the subsurface after ref. [5]. Note that points taken within 5 μm of the glass surface have an uncertainty of up to 20% with all other points between 5 and 10%. The lines are a guide to the eye.

relaxation (aided by water diffusion) separately from the bulk by using a more rapid surface stress relaxation time. The second model will treat the bulk stress relaxation time as a function of gradually varying water content in the glass surface region, with a shorter relaxation time corresponding to locations with a greater concentration of water.

2. Surface stress relaxation during ion-exchange

It has been observed previously that glass fibers heat-treated in a two-point bend configuration in the presence of water vapor at a temperature below the glass transition temperature retain measurable curvature upon release of the bending stress. This effect has been attributed to surface stress relaxation accelerated by water diffusion, resulting in the formation of a residual stress upon release of the bending stress. A simple method was developed to calculate the effective surface stress relaxation diffusion coefficients [12–14].

Surface stress relaxation takes place at a faster rate than bulk stress relaxation in the presence of water, presumably due to a lowered viscosity of the glass surface that is affected by water [11]. In this section it will be shown that molten KNO_3 salt loses weight if heat-treated prior to melting and that silica fiber can be permanently bent in the molten salt at temperatures employed during ion-exchange strengthening of glass. These observations indicate the presence of a non-negligible amount of water in the molten salt, and therefore surface stress relaxation, is possible during the ion-exchange strengthening process. Recently, it was shown that a dried sodium aluminosilicate glass exhibited an increased surface hydrogen content after being heated in molten $NaNO_3$ [15] or molten KNO_3 [16], indicating water entry during alkali ion-exchange and supporting the present hypothesis.

Studies of the surface stress relaxation kinetics of a soda-lime silicate glass were also conducted to estimate surface stress relaxation diffusion coefficients at temperatures commonly employed in ion-exchange strengthening.

2.1. Experimental: water in KNO_3 and silica glass surface stress relaxation kinetics by fiber bending in KNO_3

A sample of granular KNO_3 (Fischer Scientific 99.3% purity) was analyzed using a thermo gravimetric analyzer (TGA), Model DTG-60/60H manufactured by Shimadzu Scientific Instruments. The KNO_3 was heated at a rate of 20 °C/min to a temperature of 200 °C and held for various lengths of time ranging from 10 to 120 min. The weight loss as a function of time held at 200 °C was determined and attributed to water evaporation.

To determine if there was an effect of salt bath water content on the surface stress relaxation behavior of silica glass, two different salt bath conditions were utilized, “wet” and “dry.” The “wet” salt bath condition was created by taking granular KNO_3 off the shelf and melting it. The “dry” salt bath condition was created by starting with the same granular KNO_3 as before, but the salt was first heat-treated at 200 °C for 16 h to dry it. Melting was done directly after drying to prevent atmospheric water vapor from readsorbing onto the dried salt powder prior to melting.

The effective surface stress relaxation diffusion coefficients of Suprasil II silica glass fibers in molten KNO_3 salt baths were obtained at selected temperatures corresponding to reasonable ion-exchange temperatures for soda-lime silicate glasses, i.e. 400 °C–450 °C. The plastic coating on the fibers was first removed by immersing the fiber in 96% H_2SO_4 at 200 °C for 5 s to obtain bare fibers with a diameter of 125 μm. The bare glass fibers were then subjected to a bending stress by placing them in silica glass tubes with an inner diameter of 1.9 cm, in a two-point bending arrangement with the two ends of a fiber being parallel and in full contact with the inner wall of the tube. The bent silica glass fibers were under a maximum tensile stress of 574 MPa, as estimated using the equation derived by Matthewson et al. [17]. These two-point bent fibers were heat-treated at 400 °C, 425 °C, and 450 °C in the two different molten KNO_3 baths, “wet” and “dry”, for various lengths of time. Silica glass fiber was employed in these experiments, rather than soda-lime silicate glass, to eliminate any effects that ion-exchange would have on the residual stress profile after heat-treatment in the salt. Furthermore, since the silica glass fiber bending kinetics were obtained earlier [12] under various temperatures and water vapor pressures, the present data can be used to estimate an equivalent water vapor pressure of the molten salt during the ion-exchange strengthening process.

Upon removal from the molten salt baths, the fibers were washed briefly with water to remove any residual salt. Then the ratio of residual radius of curvature R_0/R was determined, where R_0 is the radius of curvature of the fiber in the tube and R is the sprung back radius of curvature. Radius of curvature in two-point bending geometry is dependent on the location, s, along the fiber from the bend apex, and so the radius R at the apex during bending must be estimated. For all fibers treated here, the bending kinetics were evaluated by an angle-measurement method outlined previously [14] but briefly described here.

The simplest and most straight forward method to find R_0/R is to take a picture of the fiber and measure the angle $\Phi_{(s\,=\,L)}$ in radians that exists between the straight, non-bent portions of the fiber from the horizontal (see Fig. 2 for an illustration of the geometry). L is the total fiber length from the point of the maximum bending stress to the point where the bending stress just becomes zero [14]. This has been shown [14] to have the relation:

$$\frac{R_0}{R} = \frac{\Phi_{(s=L)}}{\pi/2}. \tag{1}$$

It has also been found from experiments that $1/R$ increases proportionately to the square root of the bending heat-treatment time t. Modeling suggests that $1/R$ increases proportionately to the surface stress relaxation depth into the fiber from its surface. Therefore, it may be inferred that the relaxation depth is increasing proportionately with the square root of the bending heat-treatment time t indicating that surface stress relaxation may be promoted by a diffusion process. Knowing that surface stress relaxation depth increases by a diffusion-controlled process, the measured radius of curvature can be related to the effective surface stress relaxation diffusion coefficient, D_s, and $r_{0,}$