Residual stress in ion-exchanged silicate glass: An analytical solution

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ABSTRACT

The ion-exchanged residual stress profile influences both the strength and the wear-resistance of glass hence its description is of great importance. Currently, residual stress profiles of silicate glasses can only be estimated by numerical time-integration based on the known ionic concentration profile and the expected stress relaxation behavior of the glass. In this work, we derived and validated the constant coefficients analytical solution describing the residual stress profile in single-step ion-exchanged glasses. The proposed solution is based on Sane and Cooper's model and assumed that both the generalized Maxwell stress relaxation function applied and that a constant ionic inter-diffusion coefficient could accurately describe the behavior of the system. Furthermore, an analytical approximation for composition-dependent stress relaxation behavior of the glass was proposed. Examples of how the newly developed analytical description of the stress profile could be fitted through regression analysis to available residual stress data were also presented.

1. Introduction

The ion exchange process occurs when a silicate glass containing mobile cation (e.g., Na^+, $Li+$) is exposed to an environment with high concentration of a different mobile cation (e.g., K^+, $Na+$). Such environment generally consists of a molten salt (e.g., KNO_3, $NaNO_3$) at a temperature high enough to overcome the activation energy for the glass inter-diffusion but lower than the strain point of the glass. As the glass sample is immersed in the molten bath, the ions near the surface diffuse out of the glass sample and are substituted by larger ions from the salt bath [1]. Due to the different ionic radii between the diffusing atoms, normally residual compressive stresses are introduced into the glass although tensile stresses would also be theoretical possible through multi-step ion exchange. In binary ion-exchange systems, the exchange cations diffuse at rates proportional to the local ionic fraction of each species. Often times, an inter-diffusion coefficient, $\overline{D}$, is used to describe the overall ion-exchange diffusion process. Although the inter-diffusion coefficient is a function of both the self-diffusion coefficients and of the local ionic fraction of each species, the Na^+-K^+ inter-diffusion coefficients in alumino-silicate (ASG) and soda-lime glasses (SLG) has been reported to be nearly constant [2,3]. Gy [4] for instance found that in SLG, the inter-diffusion coefficient at low temperatures (420–460 °C) and short exchange times (72 h) did not vary considerably, especially near the glass surface. The inter-diffusion coefficient is generally assumed to follow an Arrhenius relationship:

$$D = D_0 \exp\left(-\frac{e}{RT}\right) \tag{1}$$

In Eq. (1), D_0 (m²/s) is a material constant, e (J/mol) the activation energy, R (J/mol·K) the gas constant, and T (K) the absolute temperature of the salt bath. Based on Eq. (1), high salt bath temperatures promote high diffusion rates. At the same time, the high bath temperature induces visco-elastic relaxation in the glass hence reducing the stress build-up magnitude. It follows that both diffusion and relaxation effects need to be carefully accounted for when designing a ion-exchanged residual stress profile.

Knowledge of the residual stress field has great practical interest as the strength of the glass can be linked to both the depth of the compressive layer (DOL) and the maximum surface compressive stress (CS) of glass articles after ion-exchange. In the past, an equation in integral form (Eq. (2)) was put forward by Sane and Cooper [5] in the attempt to describe the residual stress field after ion exchange in a single step exchange bath:

$$\sigma(x,t) = -\frac{B \cdot E}{1-\nu} \int_0^t R(t-t') \frac{\partial}{\partial t'} C(x,t')dt' \tag{2}$$

The term, $C(x,t)$, stands for the ionic concentration near the surface of the glass. The terms B (wt%⁻¹), E (Pa), and ν refer to the dilation coefficient, the Young's modulus, and the Poisson ratio of the silicate glass respectively. The equation assumed that the ionic distribution function, $C(x,t)$, the Young's modulus, the Poisson's ratio, the dilation constant, and the stress relaxation function, $R(t)$, were known. Sane and Cooper's equation has been often used in the literature to describe the residual stress profile as for instance in Shen and Green [6], and recently by Seaman et al. [7]. In all cases, the equation had to be solved

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Nomenclature

A	Prony series relaxation coefficient ($\Sigma A_i = 1$) (1)
B	dilation (Cooper's) coefficient (wt%$^{-1}$)
$C(x,t)$	ionic concentration (wt%)
D	inter-diffusion coefficient (m^2/s)
e	activation energy (J/mol)
E	Young's modulus (Pa)
L	glass plate half thickness (m)
R	gas constant, 8.3145 (J/mol·K)
$R(A, t/\tau)$	constant coefficients relaxation function (1)
$\widetilde{R}(A, t/\tau, \chi)$	composition-dependent relaxation function (1)
t	exchange time (s)
T	exchange temperature (K)
x	depth from the glass's surface (m)
α	non-dimensional depth from the glass surface, $\alpha \equiv x/\sqrt{4Dt}$ (1)
ΔC	difference between surface's and before-soaking's ionic

	concentration (wt%)
$\sigma(x,t)$	residual stress due to ion exchange (Pa)
$\sigma_c(t)$	stress at center of the glass for finite thickness glass plates (Pa)
σ_0	stress at the surface of the glass for $x = 0$, $t = 0$, $\sigma_0 \equiv -B \cdot E \cdot \Delta C / (1 - \nu)$ (Pa)
γ	Euler-Mascheroni constant, $\gamma \approx 0.5772156649$.
ν	glass's Poisson ratio (1)
τ	relaxation time (s)
ξ	non-dimensional relaxation time, $\xi_i \equiv \sqrt{\tau_i/t}$ (1)
χ	proportionality constant relating the relaxation time to the ionic concentration, $C(x,t)$ (1)

Indices

i	number of terms in Prony series relaxation model
s	glass's material property at the exchanged surface
0	glass's material before exposure to salt bath

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numerically as no analytical solution was known for Sane and Cooper's equation.

Startsev [8] proposed a mathematical model similar to Sane and Cooper's to describe the stress development and relaxation in SLG during ion exchange and heat treatment. Startsev's model was shown to reflect the salient features of the temperature dependences and depth profiles of glass properties in the modified surface layer. Regretfully, Startsev's model also proved too complicated to be solved analytically. Recently Allen et al. [9] proposed a numerical computer-implemented method for predicting/estimating chemical depth of layer (DOL) and maximum surface compressive stress (CS) of glass articles after ion-exchange. The methods could be used to select glass compositions, salt bath temperatures, and/or ion-exchange times which provide desired DOL and/or CS values. Similar to their predecessors, Allen et al.'s method relies on numerical calculations to solve for the ion-exchanged residual stress distribution.

1.1. Limitations of Sane and Cooper's constant coefficients equation

In addition to not providing a closed-form solution, it was pointed out that Sane and Cooper's equation was unable to capture the same features found in experimental ion-exchanged stress profiles. For instance, although Sane and Cooper's equation displayed a subsurface stress peak, its location was at a time scale greater than observed experimentally [5,6]. Various theories have been put forward as to explain the discrepancies between Sane and Cooper's model and experimental results [2,4,6]. These theories suggested that the equation should account for the composition-dependent relaxation behavior of the glass, the densification of glass during ion-exchange, and the effect of humidity on the diffusion coefficient [7].

The goal of this work is to derive an analytical solution to Sane and Cooper's equation including any relevant composition dependent terms. No attempt was made to give a physical explanation to the processes involved in the generation of such residual stresses. In the proposed model we assumed that the glass relaxation behavior followed a finite Prony series of a generalized Maxwell model. Practically the Prony series could model not only the generalized Maxwell stress relaxation but also the relaxation behavior described by the Kohlrausch-Williams-Watt (KWW) function sine the KWW could be exactly described by the Prony series:

$$e^{-(t/\tau)^b} = \sum_i A_i e^{-t/\tau_i}, A_i > 0 \quad \forall \, i, \qquad \sum_i A_i = 1 \tag{3}$$

In the past, Rekhson [10] used the KWW model to describe the behavior of borosilicate glass (BSG) near the glass transition region.

Duffrène et al. [11] explained the inadequacies of the KWW function in characterizing the viscoelastic behavior of SLG in the temperature range 530 °C to 600 °C and suggested the use of the generalized Maxwell model, represented by the Prony series. Kadali [12] showed experimentally that a five terms Prony series of a generalized Maxwell model fitted well the shear stress relaxation data of BSG. Carbone [13] used Prony series to describe the behavior of SLG at 550 °C. Shen et al. [14] and Shen and Green [15] used the two terms Prony series (i.e., the Burger model) to describe the compressive relaxation behavior of SLG between 400 °C and 500 °C, and at 550 °C respectively. Zhou et al. [16] also found excellent agreement between the Burger model and shear creep/relaxation data of optical glass between 560 and 590 °C. Finally Lee et al. [17] also use a one term Prony series to model residual stresses in tempered SLG.

In addition to finding an analytical solution to Sane and Cooper's equation for constant coefficients, an approximate analytical solution for the residual stress profile for material non-constant relaxation time coefficients was obtained. The use of the analytical solution is expected to facilitate the analysis of experimental data compared with analysis based on numerical solutions. The obvious advantage of a closed-form solution to describe the residual stress distribution after ion-exchange is that, given a known set of material properties, it allows optimization of the exchange process. Although currently the proposed solution for the concentration dependent relaxation function could only be applied to single step ion-exchange processes, a modification version of the solution could be implemented to account for a multiple step ion-exchange glass profiles.

2. Analytical solution for residual stress distribution

In this section we present the analytical solution to Sane and Cooper's equation (Eq. (2)). Two separate cases were considered: in the first case, the time relaxation coefficients were assumed to be independent of the ionic concentration. In the second case, the relaxation time coefficients were taken as linearly dependent on the ionic concentration, $C(x,t)$. Details on the derivations of the equations are provided in Appendices A and B.

2.1. Concentration-independent relaxation function

Sane and Cooper derived an equation to describe the residual stress profile, $\sigma(x,t)$, near the surface of a semi-infinite silicate glass due to ionic exchange [5]. Such relationship (Eq. (2)) was expressed in integral form but not formally solved. The negative sign in Eq. (2) indicates compressive stress. The ionic concentration, $C(x,t)$, was assumed to be