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Simulation of surface structural relaxation kinetics in silica glass accelerated by water vapor

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ABSTRACT

It is known that surface structural relaxation of silica glass takes place more rapidly than bulk structural relaxation, especially in the presence of water vapor. The effect of water vapor pressure, heat-treatment temperature and initial fictive temperature on the surface structural relaxation kinetics in silica glasses was investigated by measuring the change of the surface fictive temperature determined from the IR reflection peak shift of silica structural bands. The superimposed component of bulk structural relaxation was subtracted from the measured surface structural relaxation data to isolate the true surface structural relaxation kinetics. The obtained surface structural relaxation data as a function of fictive temperature, heating temperature and water vapor pressure were simulated with a model based on the diffusion equation with time-dependent surface concentration. The simulation model was used to predict the surface structural relaxation kinetics of the optical fiber having a high fictive temperature of ∼ 1650 °C at 950 °C under 355 torr of water vapor, and it was confirmed that the present model can simulate surface structural relaxation of the fiber reasonably well.

1. Introduction

Properties of a glass at room temperature vary with its fictive temperature. For example, silica glass with a higher fictive temperature shows higher density [1–3], a higher refractive index [1,2], a higher etching rate with HF [4], higher hardness [5] and a higher Young's modulus [6]. Fictive temperatures and their corresponding glass properties can change with time in the glass transition temperature range by the process of structural relaxation. Therefore, in order to predict glass properties after a heat treatment one has to understand relaxation kinetics.

It has been observed that surface structural relaxation can take place much more rapidly than bulk structural relaxation, especially in the presence of water vapor [7–10]. This phenomenon is expected to play an important role in glass products with large specific surface area such as fibers and micro-lenses.

Earlier studies showed that the surface structural relaxation propagates into a glass as a diffusion process [7]. The effective diffusion coefficient, D, for surface structural relaxation has been determined by Davis [8] and Davis and Tomozawa [7] using thin films of thickness around ∼100 μm of various silica glasses as a function of temperature under 355 torr of water vapor. In their method, they measured the time dependence of structural relaxation of the thin films by the IR absorbance and obtained the diffusion coefficient by comparing the data with the equation for diffusion uptake, M, given by

$$\frac{M}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(-D\frac{(2n+1)^2\pi^2 t}{4l^2}\right), \qquad (1)$$

where M_∞ is the equilibrium value of the total amount of uptake and l is the half thickness of the plate [11].

Agarwal [9] and Agarwal and Tomozawa [10] also determined the diffusion coefficient from the relaxation kinetics study of thin silica films by IR absorption. In their study, because of the sample's lower viscosity compared with other silica glasses, bulk structural relaxation was superimposed on the surface structural relaxation and they separated these two contributions by measuring the relaxation kinetics of the silica glass film samples of different thicknesses. Agarwal [9] also obtained the diffusion coefficient of surface structural relaxation of the glass by measuring the relaxation depth profile of thick samples by IR reflection combined with successive etching and comparing the diffusion profile with the

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complementary error function. These two different methods gave consistent values of the diffusion coefficient for surface structural relaxation. However, in these analyses, the boundary condition of the constant surface concentration was employed. While the method is useful to estimate the depth of structural relaxation by the surface structural relaxation, it does not simulate the change of the extent of the relaxation of the glass surface, which can be probed by IR reflection, since the extent of the relaxation on the surface is time-dependent.

Recently, using the boundary condition of time-dependent surface concentration, the surface structural relaxation was analyzed [12]. As a result, it was found that the surface structural relaxation kinetics depend upon the size and shape of the glass: for example, the surface of a fiber relaxes faster than surface of a thick plate in the same water vapor pressure at the same temperature even though they have same glass composition and same initial fictive temperature.

Specifically the structural relaxation kinetic at the specimen surface can be obtained from the time dependence of the fictive temperature of the surface. Fig. 1(a) shows a schematic diagram of time variation of normalized diffusion concentration profile with boundary condition of time-dependent surface concentration. Here, $C(x,t)/C_0$ represents the concentration at position x and time t, normalized with the initial concentration. This corresponds to the normalized fictive temperature variation. This diffusion profile can be obtained when the surface diffusion flux is given by

$$J(0,t) = \alpha(C_0 - C_S), \tag{2}$$

where α is the proportionality constant between the diffusate flux, J, at the specimen surface at time t, and the difference in actual concentration at the specimen surface, C_S, and initial concentration of the sample, C_0. Relaxation kinetic at the specimen surface can be observed as time dependence of the normalized fictive temperature on the surface, which corresponds to C_S/C_0, as shown in Fig. 1(b). Under this boundary condition, surface concentration in a plate sample, which corresponds to a normalized function of the surface structural relaxation, is expressed by [12]

$$\frac{C_S}{C_0} = 1 - \exp\left(\frac{\alpha^2}{D}t\right)\operatorname{erfc}\left(\sqrt{\frac{\alpha^2}{D}t}\right) \tag{3}$$

and in a fiber sample by [12]

$$\frac{C_S}{C_0} = 1 - \sum_{n=1}^{\infty} \frac{2(a\alpha/D)}{\beta_n^2 + (a\alpha/D)^2} \exp(-\beta_n^2 Dt/a^2), \tag{4}$$

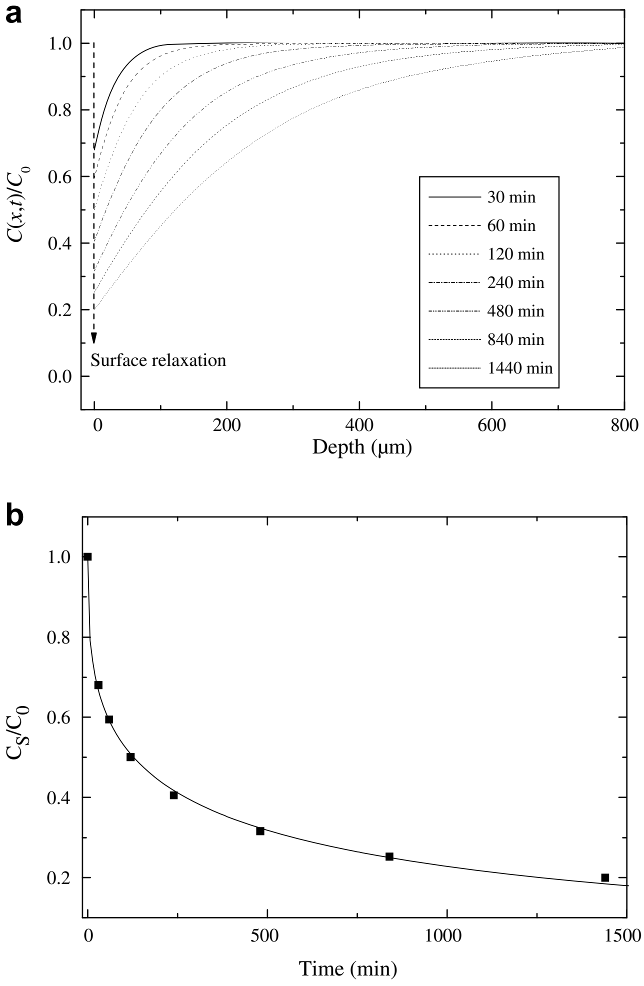

Fig. 1. Schematic diagram of time variation of normalized concentration profile under boundary condition of time-dependent surface concentration [12]. (a) Normalized concentration profile with boundary condition of time-dependent surface concentration and (b) normalized surface concentration as a function of time (initial fictive temperature = 1200 °C, heat-treatment temperature = 950 °C, in 355 torr water vapor).

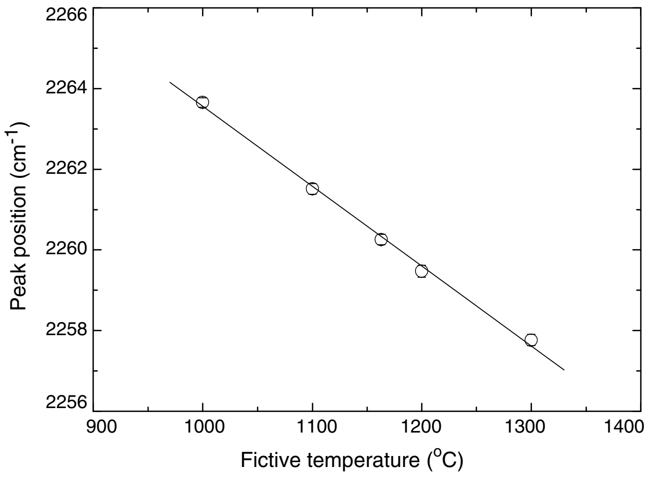

Fig. 2. Relationship between the IR absorption peak wavenumber around ~2260 cm^{-1} and the fictive temperature for the silica glass. The straight line is a linear regression fit to the data [15].

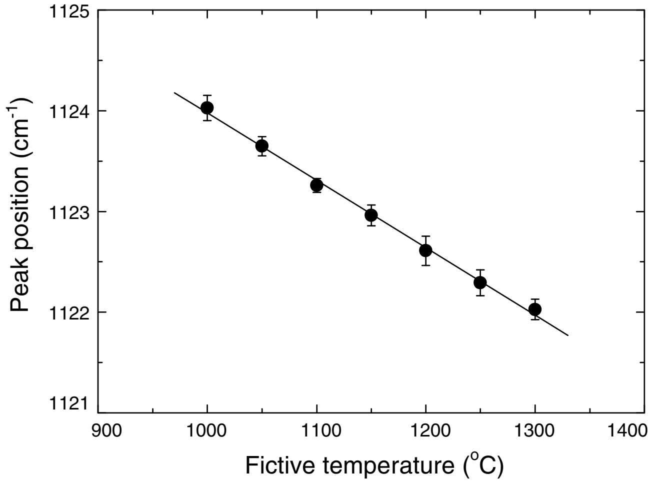

Fig. 3. Relationship between the IR reflection peak wavenumber around ~1123 cm^{-1} and the fictive temperature for the silica glass. The straight line is a linear regression fit to the data [16].