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RESEARCH ARTICLE

Correlations between residual stress and water diffusion in silica glass at low temperatures

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Abstract

Residual stress profiles in silica glass were measured after water diffusion treatment under 47.33 kPa (355 Torr) water vapor at 350°C and 650°C. Earlier, it was found that water solubility in silica glass exhibited peculiar time dependence: Solubility increased with time exceeding the normal water solubility expected from higher temperatures. Then, the water solubility decreased with time. It was hypothesized that the stress induced by water diffusion and its subsequent relaxation is responsible for the phenomenon. Residual surface stress generation in silica glass was found to correlate closely with surface hydroxyl concentration, systematically increasing until eventual surface stress relaxation results in stress decrease for treatments beyond 265 hours at 650°C. This observation validates previous theories of time dependent diffusivity in silica glass.

KEYWORDS
glass, silica, birefringence, diffusion/diffusivity

1 | INTRODUCTION

Diffusion of water in silica glass has been frequently studied and is known to be sensitive to environmental changes such as temperature and ambient water vapor,[1–3] as well as impurity compositions and applied strain.[4,5] Water diffuses as molecular water, H_2O, which reacts with the glass network to form immobile hydroxyl, OH, groups by the following reaction[6]:

$$\equiv Si - O - Si \equiv + H_2O \rightleftarrows \equiv SiOH + HOSi \equiv \tag{1}$$

At high temperature the reaction takes place rapidly, and reaches the local reaction equilibrium and its effective diffusion coefficient can be given:

$$D_{eff} = 4\,[OH]\,D_{H_2O}/K \tag{2}$$

where K is the reaction equilibrium,

$$K = [OH]^2 / [H_2O] \tag{3}$$

D_{H_2O} is molecular water diffusion coefficient and $[OH] \gg [H_2O]$.

Solubility of a gas, e.g. He, in glass is represented as by C_i/C_g, where Ci is the concentration of gas dissolved in glass and C_g is the concentration of molecules in gas phase.[7] In the case of water in glass, C_g is expressed as the water vapor pressure in the experimental environment, e.g. 355 Torr, while C_i is H_2O weight fraction equivalent of [OH] concentration in glass, since most of H_2O in glass reacts with glass forming OH. Equilibrium of water in glass is reached at temperature above 850°C. Below 850°C, due to delayed stress relaxation, the equilibrium was not reached.

Previous works have characterized water diffusion through measurement of OH concentration profiles in low-water silica glass.[2,8,9] At very low temperatures, below 550°C, surface OH concentration increases toward an

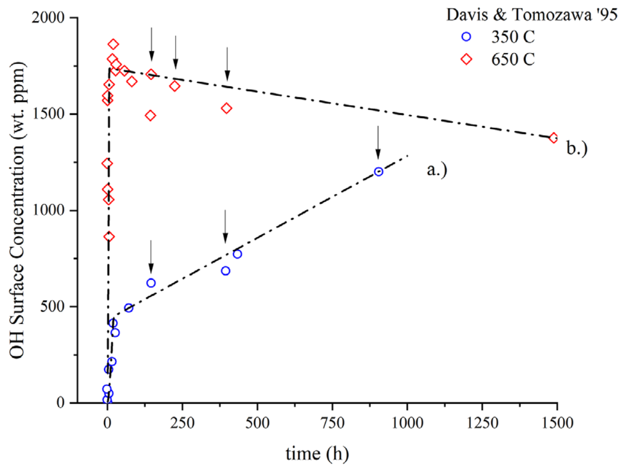

FIGURE 1 Surface OH concentration measured in silica glass following successive heat treatment at a.) 350°C and b.) 650°C in a 47.33 kPa (355 Torr) water vapor. Adapted from Davis and Tomozawa.[2] Arrows indicate heat-treatment times where residual stress profiles were collected

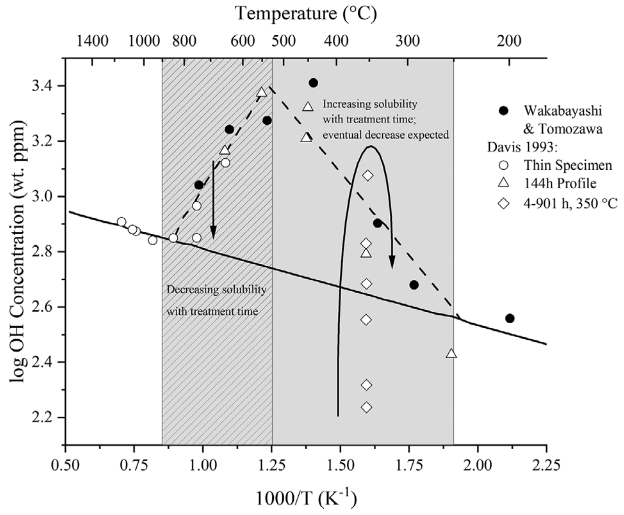

FIGURE 2 Log solubility of OH concentration as a function of heat treatment temperature in a 47.33 kPa (355 Torr) water vapor environment. Solubility of the glass interior was shown to exhibit the same behavior as surface concentration. Adapted from reference[1,10]

equilibrium concentration over several hours. Between 550 and 850°C, surface OH concentration is seen to increase beyond equilibrium value, extrapolated from higher temperature values, then decreasing toward the expected concentration based on higher temperature data. It has been proposed that this is due to initial compressive stress generation from water diffusion, which drives the reaction (1) to the right, followed by surface stress relaxation which drives the same reaction (1) to the left[8] (see Figure 1, line (b)). These characteristics are summarized in Figures 1 and 2.

This hypothesis appears to be consistent with the effect of applied bending stress on water diffusion in SiO_2 glasses.[4,5] Nogami and Tomozawa[4] showed that the water solubility in silica glass is higher under compressive bending stress and lower under tensile stress at 192°C and 350°C. Agarwal et al[5] subsequently showed that water solubility was higher under compressive stress and was lower under tensile stress at 250°C, while water solubility at 650°C was higher under compressive stress for short times, eventually reversing at longer heat treatment time.

In the present work, residual stress profiles of silica glass were measured as a function of water diffusion time using photoelastic techniques and were compared with previously obtained OH concentration profiles in order to verify the theory of stress buildup and relaxation during low temperature heat treatments. The previously obtained OH profiles were generated within a similar glass composition using identical heat treatment times, temperatures, and environmental conditions.[2] Said OH profiles were measured via IR spectroscopy in concert with successive etching of thin silica plates. Where feasible, the stress measurement parameter space was expanded to compare with collected point measurements of surface OH concentrations as a function of heat treatment time beyond the full profiles provided.[2]

2 | EXPERIMENTAL PROCEDURE

2.1 | Sample preparation

Low water silica glass samples were cut from optical fiber preform (Furukawa Electric Co.) containing < 0.1 wt. ppm of OH and 1000 wt. ppm of Cl. This glass is similar to Type IV according to the classification by Bruckner[11] The glass transition temperature has been reported as 1096°C.[12] Samples were cut into rectangular prisms of 10 mm × 10 mm × ~75 mm and polished on two of the long parallel surfaces with shaded planes with 10 mm × 75 mm (see Figure 3a). Polishing was performed using a progression of silicon carbide paper from 240 to 1000 grit followed by a final polish using cerium oxide in distilled water. Samples were then annealed at T_g for one hour in lab air at ~1 kPa (~7 Torr) water vapor pressure and left to furnace cool. To remove potential surface crystallization due to annealing, the sample was etched in 48% HF for 60 seconds to remove ~1 μm from all of the surfaces. Before polishing, all samples had a cross section of ~10mm × 10 mm. After processing, the samples had a cross-section of ~7 mm × 10 mm (see Figure 3a).

Samples were heat-treated successively from 100 to 900 hours in an environment of constant partial water vapor

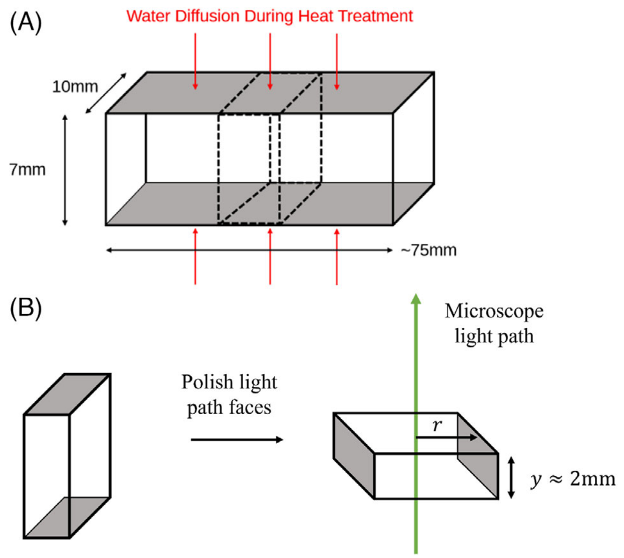

FIGURE 3 (a) Schematic of silica parent sample with the surface polished before heat treatment indicated with shading and approximate dimensions. An interior section is removed for characterization as indicated by the dashed lines. Incremental heat-treatment and thus water diffusion can be evaluated by subsequent sectioning. (b) Polishing of the cut cross section, and retardance measurement of said cross section is performed perpendicular to the diffusion surface or interest. Dimension y is the cross-section thickness (~2 mm) and r is the direction of diffusion cross section, measured from the shaded surface inward.

pressure of 47.33 kPa (355 Torr). The temperatures of 350 and 650°C were chosen in order to compare stress profiles with previous OH concentration measurements.[2,9,10] In order to measure the stress profile of the sample cross section, a 3 mm-thick child sample was cut from the main piece and the cross section was polished perpendicular to the previously polished diffusion surfaces using the same procedure and resulting in a final child sample average thickness of 1.8 ± 0.3 mm (see Figure 3b). The dimension of the "child" sample was chosen in order to allow for sufficient distance between the internal cross section and the edges and vertices of the "parent" sample which would be undergoing the successive heat treatments. This assures a reasonable assumption of a one-dimensional diffusion profile from the middle of the cross-section edge inward (indicated by the r-direction in Figure 3b), in which the diffusion distance is significantly smaller than the dimensions of the sample.

2.2 | Stress measurement

Stress profiles near the glass surface were measured using a polarized light microscope (Nikon Eclipse LV100N POL) via the Sènarmont technique for retardance measurement (see Figure 4).[13–16] Samples are immersed in an index-matching fluid to mitigate surface reflection of incident light (see Figure 5). Retardance was then measured as a function of position within the glass. Retardance is related to residual stress by the stress-optic law:

$$\sigma(r) = \frac{\Delta(\mathrm{r},\ \theta)}{C \cdot y} \tag{4}$$

Where Δ is the retardance in nm, C is the stress-optic coefficient of the material in Brewsters $[10^{-12} \cdot Pa^{-1}]$, and y is the path length through the material in mm. Retardance is found via rotation of the microscope analyzer incrementally to determine the minimum transmitted intensity at a given point in the material. Retardance is then proportional to this angle and the wavelength of the microscope light source:

$$\Delta\ (r,\ \theta) = \frac{\lambda \cdot \theta_{min}(r)}{180°} \tag{5}$$

The stress optic coefficient is approximated as 3.0 Brewster to estimate the magnitude of residual stress.[17] Stress as a function of position, $\sigma(r)$, can accordingly be calculated by Equation (4). The spatial resolution of the stress measurement is limited by the resolution of the camera and microscope optics to about ± 0.2 μm. This is similar to the resolution of the OH depth profiles obtained by Davis, where successive etching of silica with dilute HF produced point measurements of OH concentration with a resolution of ± 0.5 μm. The OH concentration profile was then measured from the change in these point measurements, resulting in an OH profile resolution of about ± 0.75 μm.[10] Calculated stress profiles were then used to determine stress generation and relaxation kinetics and compared with previously obtained OH diffusion profiles.

3 | RESULTS

Residual stress parallel to the glass cross section surface was calculated as a function of distance from the diffusion surface using the measured retardance values (see Figure 6). At equivalent heat treatment times, compressive stress was found to increase with successive 350°C treatments up to 900 hours, similar to the trend seen in surface OH concentration (see Figure 7). Both surface OH concentration and surface residual stress are observed to decrease at long times at 650°C (see Figure 8). At this higher temperature, surface stress is observed to relax on a similar timescale as OH concentration decrease, although the relaxation occurs more quickly. Along with a surface compressive stress, at 650°C an interior tensile stress

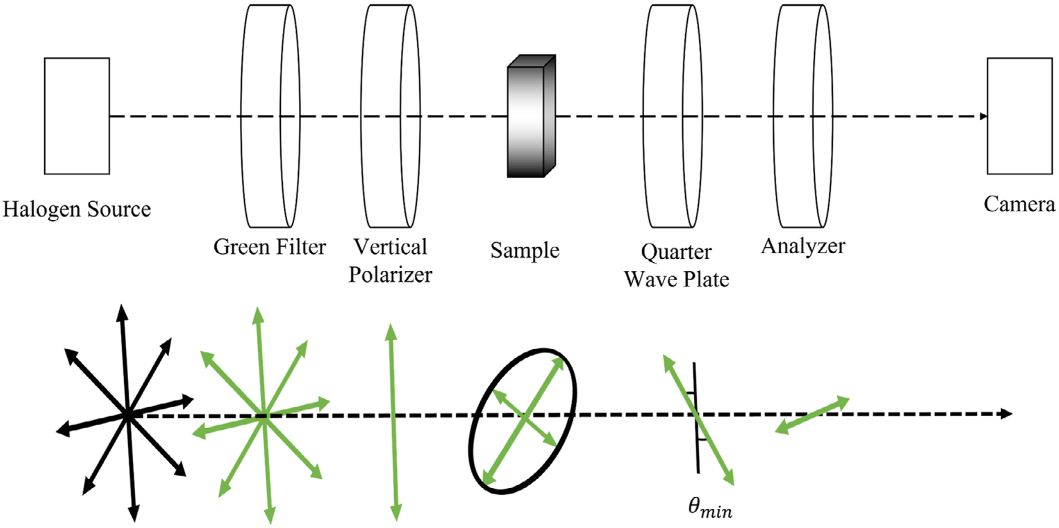

FIGURE 4 Schematic of the microscope configuration used for retardance measurement with the Sènarmont method. The optical components are shown above with the polarization state of the light shown schematically below. Elliptically polarized light is output form the sample which is at 45 degrees to the incoming polarized light. The difference in semimajor axes is proportional to the birefringence. Analyzer angle θ is incremented to find the minimum intensity resulting from a rotation of polarized light by the quarter wave plate, and thus retardance via Equation (5)

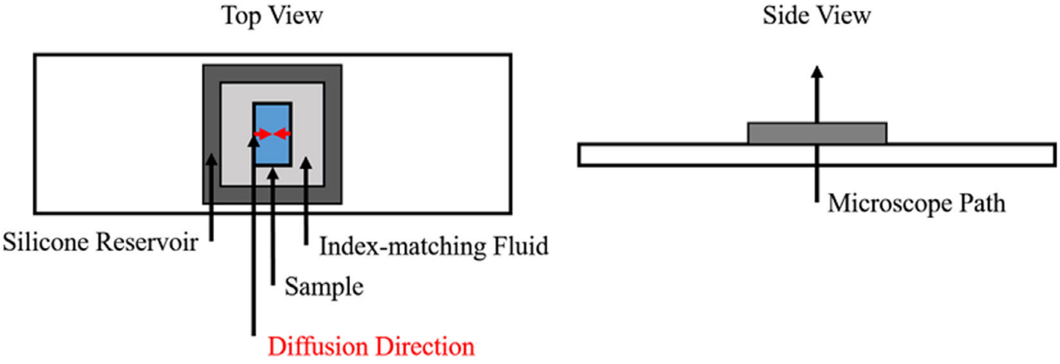

FIGURE 5 Experimental configuration during retardance measurement following heat-treatment illustrating orientation between the microscope and sample fixture. The sample is indicated in the center and measures roughly 10 mm × 7 mm × 2 mm. Diffusion direction during heat treatment is indicated by arrows within the sample along the r axis defined in Figure 2

was observed, indicating temperatures are high enough for a structural deformation to occur at this timescale without significant change in water content deep within the glass. The interior zero-stress point is observed to correspond approximately with the previously measured depth of OH diffusion at the same heat treatment times (see Figure 8). These correlations are summarized in Figure 9 in which the surface stress is compared to the surface OH concentration as a function of time. At shorter times, which do not correspond to available OH concentration profiles, the data has instead been compared to previously reported point measurements of surface OH concentration.[2]

4 | DISCUSSION

The correlation between surface residual compressive stress and surface OH concentration is consistent for both temperatures, although at the higher temperature there is a more rapid relaxation than there is a decrease in surface OH concentration. Because fast relaxation at the glass surface has been observed at temperatures as low as 200°C, stress buildup in this work must be occurring more rapidly than relaxation in order to observe the initial increase.[8] Upon reaching sufficient OH content and sufficiently decreased relaxation time, further stress increase may no longer outpace relaxation even at lower temperatures,

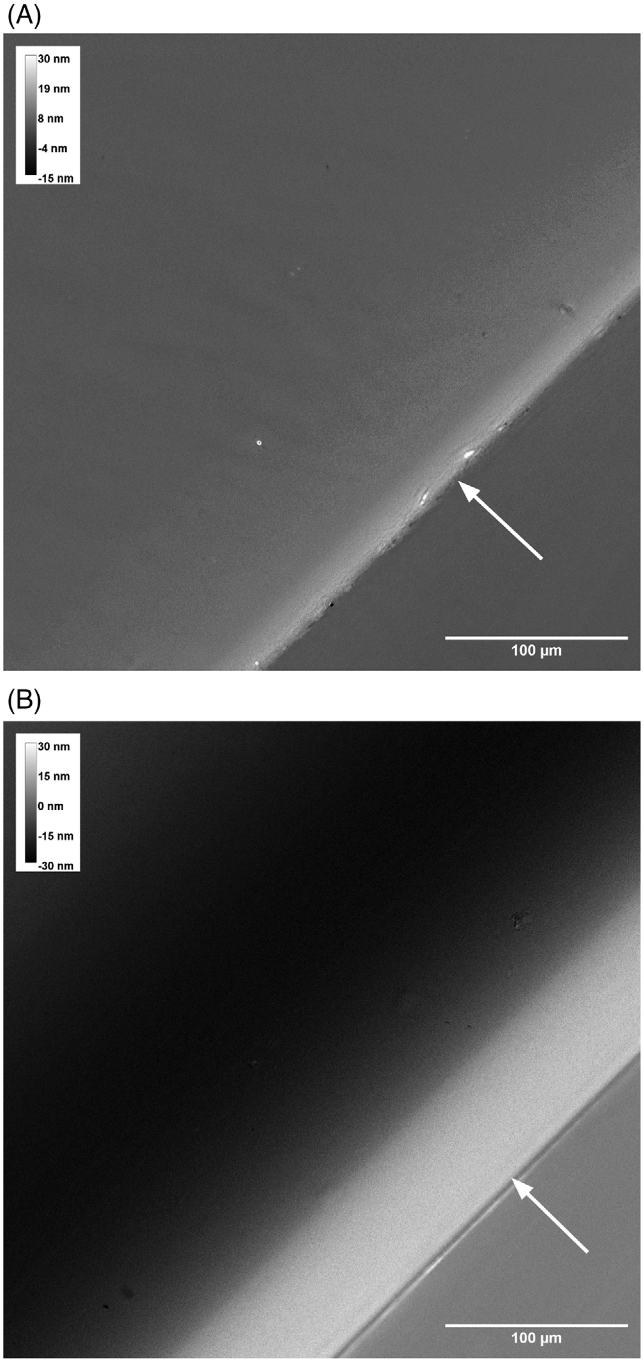

FIGURE 6 Retardance map of silica glass sample surfaces for samples heat-treated for 400 hours at 350°C (a) and 650°C (b). Glass surface is indicated with an arrow with the water diffusion into glass proceeding in the direction of the arrow (along coordinate *r*)

producing the eventual decrease in surface compressive stress observed only at the higher temperature within the experimental timescale. This is likely a cause of time-dependent diffusivity of water in silica glass.[1,8] Although the compressive stress generated by water diffusion into silica glass can promote the reaction between silica glass and water molecule, the reaction is not instantaneous.

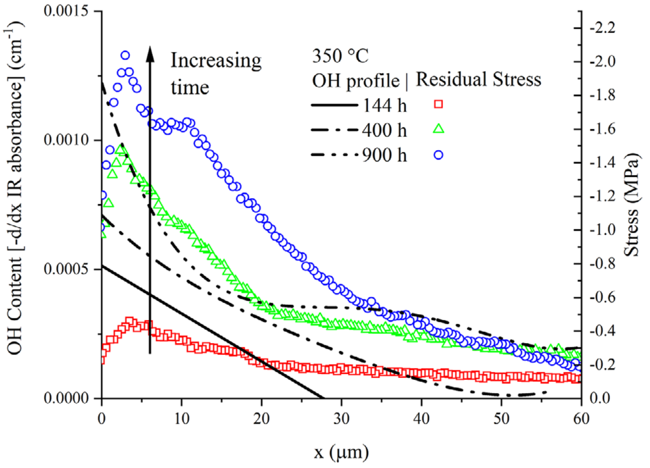

FIGURE 7 Residual stress profiles plotted alongside OH concentration profiles for 350°C. OH concentration profile adapted from Davis[10]

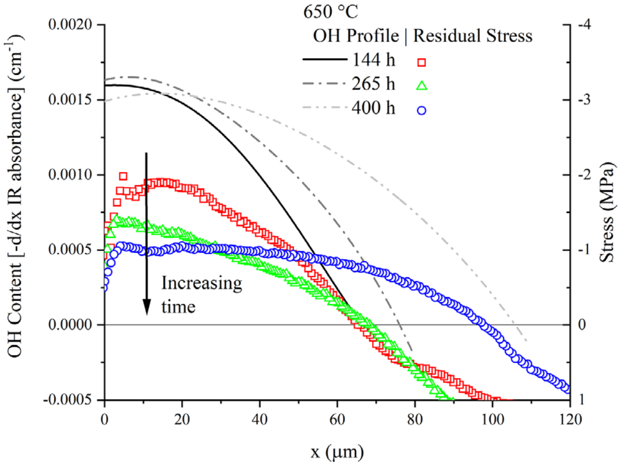

FIGURE 8 Residual stress profiles plotted alongside OH concentration profiles for 650°C. OH concentration profile adapted from Davis[10]

Therefore, the compressive stress profile may precede the hydroxyl concentration profiles. The two profiles may not exhibit the same time and position profiles.

5 | CONCLUSIONS

Low-temperature, long-time heat treatments of silica glass were found to result in residual stress buildup in a humid atmosphere of 355 Torr partial water vapor pressure at 350 and 650°C. At both temperatures, residual stress was analyzed using photoelastic techniques and was found to correlate well with diffusion depth of OH groups in the glass network. At 650°C surface compressive stress begins to decrease at a similar rate as surface OH content, implying a relation between residual stress relaxation and

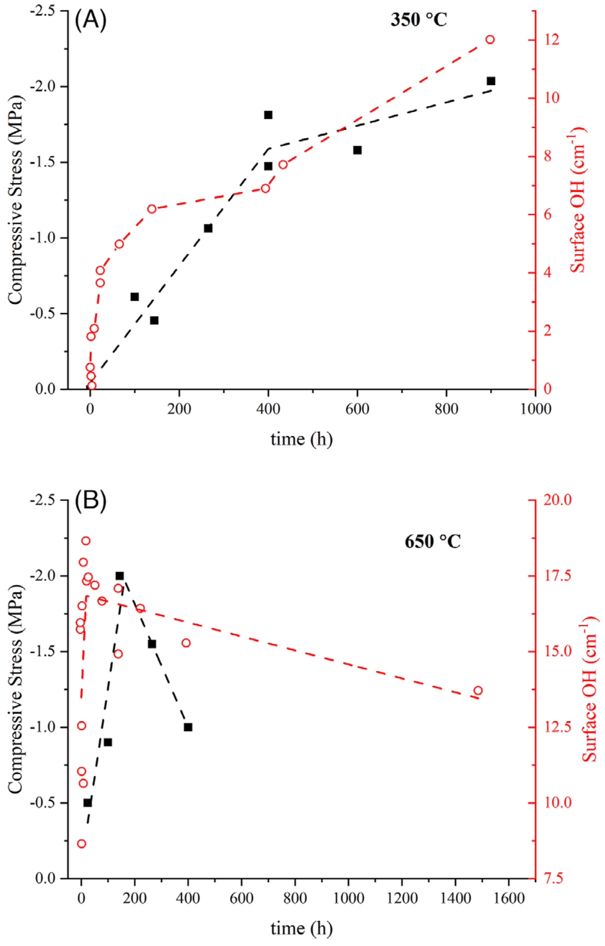

FIGURE 9 Comparison of surface residual stress (closed points) and surface OH content (open points) within the first 0.5 μm of material as a function of heat treatment time for 350°C (a) and 650°C (b). Surface OH concentration adapted from reference[2]

equilibrium OH concentration. The observed residual stress is likely the cause of previously measured time-dependent diffusivity in silica glass over similar temperature ranges.

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