Hydrothermal reactions of soda lime silica glass – revealing subsurface damage and alteration of mechanical properties and chemical structure of glass surfaces

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Abstract: Hydrothermal treatment provides a unique way to reveal subsurface damage of soda lime silica (SLS) float glass. During the hydrothermal treatment, the penetration of water, ion-exchange, and hydrolysis reaction can take place. These reactions are accelerated at locations where subsurface damage exists. Interestingly, the hydrothermally-treated glass surface exhibits higher fracture toughness, lower hardness, and less resistance to mechanochemical wear at high humidity compared to the pristine SLS float glass. These property changes can be explained by the leaching and polymerization of the silicate network and the chemical environment of hydrous species in the surface region of SLS glass.

Keywords: hydrothermal reaction; subsurface damage; soda lime silica glass; water penetration; hydrous species; mechanical properties

1. Introduction

The surface and subsurface damage of soda lime silica (SLS) glass can affect the strength and durability of the glass.[1–4] Such damage can be created when contact stresses are applied to the glass surface during the manufacturing, handling, and storage, but the severity of damage can be mediated through environmental effects. For example, adsorption of a monolayer of lubrication molecules on the surface can prevent physical wear at the sliding interface whereas interfacial shear in the presence of reactive molecules will damage and degrade the surface.[5,6] The history of normal indentation or interfacial shear at the surface can lead to a distribution of local chemical structures and residual stresses.[7–10] In the case of sharp cracks, tensile residual stress is believed to be present and, in humid environments, the crack will propagate in the direction where this residual stress is largest.[11] Changes in the stress profile in the surface region at the vicinity of the crack tip can be accompanied by changes in the chemical structure.[12] While it is generally accepted that these phenomena can be explained by stress corrosion mechanism,[13–15] revealing the subsurface damage and understanding their effect on mechanical properties and mechanochemical behavior is still challenging.

This study describes a method to reveal subsurface damage without using strong acid or base etching. Wong et al. showed that HF can be used to reveal subsurface damage on fused silica by controlling the etching rate precisely.[16] In this case, HF etching treatment reveals the subsurface damage at the cost of destroying the entire glass surface.[17] Since the subsurface damage is accompanied by residual stress which strains the silicate network, it is hypothesized that the associated strained bonds will preferentially react with water molecules. Here, it is shown that if reactions between the SLS glass surface and water are accelerated through

hydrothermal treatment, the residual stress and related chemical structures can be etched selectively to map the damage on the surface.

Another outcome of this study was the observed alteration of mechanical properties and the mechanochemical response due to the hydrothermal leaching and hydration of the surface. For example, if the sodium ion leaching creates a softer layer or region on top of the bulk glass, indentation loading and unloading along the surface normal direction will be altered since the surface layer will be compacted and absorb more mechanical energy.[18] Recently, SLS glass has been found to show very unique wear resistance in high relative humidity environment.[5] While the mechanism of such mechanochemical wear behavior is not fully understood yet, the wear resistance was found to be related to the presence of sodium ions associated with the silicate network of SLS glass. The glasses without leachable sodium ions such as fused quartz, alkali-free display glass, and borofloat do not show the same wear resistant behavior at high humidity.[19,20] In aluminosilicate glasses where sodium is associated with aluminum tetrahedral sites instead of non-bridging oxygen in silicate network, the wear resistance at high humidity is not observed.[4] While removing the sodium ions from the surface region of SLS glass through thermal poling also removes the wear resistance effect of SLS glass, the silicate network is also altered drastically.[18] Therefore, a means to leach sodium out of SLS glass with no or minimal change in the subsurface network is needed to investigate the effect of sodium ions in mechanochemical wear resistance of the SLS glass.

In order to achieve these goals, hydrothermal reactions of SLS glasses were studied. Hydrothermal reactions are typically carried out in a sealed reactor at temperatures higher than 100 °C.[21] During the hydrothermal treatment at 200 °C and 250 °C, water can diffuse into alkali-free glasses and react forming Si-OH groups.[22,23] Such hydrothermal treatments in

liquid water have been reported to strengthen a vitreous silica glass.[22,24] In the case of SLS glass, hydrothermal treatment in liquid water was reported to create a porous surface layer.[25] Our study investigated the effect of hydrothermal treatment in the vapor phase around 150 °C with the focus on the aforementioned goals – revealing the subsurface damage; studying mechanical properties of the modified surface layer; and investigating how the wear behavior is affected by sodium ion leaching. It should be noted that liquid water and water vapor have the same reactivity in hydrothermal reactions since their chemical potentials are the same at this saturated condition. However, transport properties in the vapor phase - especially the removal of reaction products from the glass - would be different than for the liquid phase.

2. Experimental Details

SLS float glass with a 1mm thickness from Asahi Co. (Asahi Co., Tokyo, Japan) was used in this study. The bulk composition of SLS (weight %) was found to be 72.3% SiO₂, 13.3% Na₂O, 7.7% CaO, 1.9% Al₂O₃, 4.4% MgO, 0.3% K₂O, and 0.1% Fe₂O₃ from X-ray fluorescence (XRF). During the manufacturing process, SO₂ treatment was applied after the glass was lifted from the tin bath onto the rollers, and this dealcalized the surface. This study investigated the air side of the float glass only because it is more pristine and defect free initially.[26]

The vapor-phase hydrothermal treatment system is schematically shown in Figure 1. It was performed in a sealed stainless steel vessel with a volume of 100 cm³. 10 mL of miliQ water was placed in the bottom of the vessel that was rinsed with ethanol and water before each treatment. The amount of water was enough to create saturated vapor between 100 °C and 200 °C in the sealed vessel. At 150°C, the saturated water vapor pressure is 0.48 MPa. The actual

temperature of the vessel was monitored with a thermocouple. All samples were cut in $2\text{ cm} \times 2\text{ cm}$ and placed on an elevated sample stage in the vessel so that the glass would interact with saturated steam only. The sealed vessel was then put in an oven set to a desired temperature. After the hydrothermal treatment, the sealed vessel was rapidly cooled with running water. The treated samples were cleaned with miliQ water, pure ethanol and UV-ozone before any mechanical tests and surface characterizations.[27]

Figure 1. Schematic representation of vapor-phase hydrothermal treatment of SLS glass at temperatures higher than $100\text{ }^{\circ}\text{C}$.

Specular reflectance infrared (SR-IR) spectroscopy was carried out with a Bruker Hyperion 3000 Microscope (Bruker, Co.) with a $15\times$ objective lens. A gold mirror was used as a reference background. Attenuated total reflectance infrared (ATR-IR) spectroscopy was performed with the same IR microscope equipped with a Ge ATR crystal accessory with 60° incident angle. Sum frequency generation (SFG) vibrational spectroscopy was used to study the chemical environment of hydrous species in the surface region of SLS glass. The detailed description of the SFG system can be found elsewhere.[28] In brief, visible laser pulses (532 nm)

from a 27 ps Nd:YAG laser and tunable IR pulses (2.5-10 μm) from an optical parameter generator and amplifier were spatially and temporally overlapped on a glass surface of interest. The incident angles of visible and IR pulses were 60° and 56° with respect to surface normal, respectively. The SFG signal was collected in a reflection geometry at the angle determined by the phase matching condition of the SFG process. The polarization combination used in this study was *s* for SFG signal, *s* for 532nm laser pulses, and *p* for IR laser pulses (*ssp*).

The surface composition of SLS before and after hydrothermal treatment was analyzed with X-ray photoelectron spectroscopy (XPS). A Kratos Analytical Axis Ultra spectrometer (Chestnut, NY) fitted with a monochromatic $\text{AlK}\alpha$ (1486.6 eV) X-ray source was used. Survey scans of O 1s, Na KLL, Ca 2p, Mg KLL, C 1s, Si 2p peaks and high-resolution narrow binding energy of O 1s and C 1s peaks, were conducted at 80 and 20 eV pass energies, respectively. The binding energies of all elements were corrected with the adventitious alkyl peak at 285 eV. The surface composition was determined after removing the adventitious carbon and carbonate species on the glass surface.[29]

Nanomechanical properties including elastic modulus and hardness of the hydrothermal treated surface were obtained using a nanoindenter (Hysitron TI 950, Minneapolis, MN) equipped with a Berkovich tip. The nanoindentation measurements was performed with displacement control. The maximum penetration depth was held at 50 nm, 100nm, 150nm and 200nm for 2 seconds. The loading and unloading rate were both 20 nm/s. The results are averaged from more than 40 indentations for each indentation depth. Vickers indentation was performed with a microindenter (MHT Series 200; Leco Corporation, St. Joseph, MI). The duration time at maximum load was 15 seconds. The Vickers hardness was averaged from more than 15 measurements for each sample. The duration at maximum load for both nanoindentation

and Vickers indentation are small enough that influence from indentation creep effect will not be significant.[30] Wear test was done using a custom-designed ball-on-flat tribometer with an environment control capability. All wear tests were conducted with 0.2 N normal force and 400 reciprocating sliding cycles. The ball used in this test was a borosilicate ball with 2.4 mm diameter (McMaster-Carr Products Inc., Elmhurst, IL). The contact pressure was calculated to be 350 MPa based on Hertzian contact mechanics. “Invisible” wear tracks, tracks that did not undergo plastic deformation during the reciprocating shear loading, were created by performing the wear test in n-pentanol vapor environment.[5,31] The wear tracks before and after hydrothermal treatment were analyzed with an optical profilometer (Zygo NV7300, Middlefield, CT).

3. Results and Discussion

3.1 Selective etching of regions with subsurface damage or residual stress via vapor-phase hydrothermal reaction

Stress corrosion is a phenomenon that accelerates hydrolysis reactions of glass upon application of mechanical stress to the glass;[14,32,33] a similar effect could be expected when a glass with residual stress is exposed to hydrolysis reaction conditions. The subsurface damage could be associated with subsurface defects such as non-bridging oxygen (NBO), three-coordinated silicon, and strained silica tetrahedron.[34] It was hypothesized the hydrothermal treatment can reveal the residual stress in the surface region since the defect sites or areas would react more readily with water at high temperature and pressure. To test this hypothesis, we ran two control tests: (i) hydrothermal reactions of the surface subjected to interfacial shear and (ii)

hydrothermal reactions of an indentation crack. The diffusion and chemical reactions of water can lead to selective etching of these defective regions without using any chemical etchants such as strong alkali or hydrofluoric acid.

Figure 2. Optical profilometry of SLS glass surface slide tracks produced in n-pentanol VPL environments (a) before and (b) after hydrothermal treatment at 150 °C for 24 hours; (c) cross-section line profiles of the wear tracks marked with dashed lines in (a) and (b).

It is known that as long as the bulk can support the applied load, the ‘visible’ wear of the glass surface can be suppressed by continuous adsorption and replenishment of alcohol molecules from the vapor phase.[5,20,31] This is called vapor phase lubrication (VPL). The key for the success of VPL is to avoid detrimental reactions at the sliding interface that can induce chemical wear of the surface. Although the formation of visible wear tracks can be suppressed in

VPL, the interfacial shear under a high normal load (~350 MPa in the test condition used in this study) could leave some damage in the subsurface glass network. Figure 2 demonstrates how this “invisible” wear track with subsurface damages can be revealed by hydrothermal treatments. Figure 2a and 2b compare the optical profilometry images of the same wear track before and after hydrothermal treatment. Figure 2c compares the cross section of wear tracks before and after hydrothermal treatment. The wear track became approximately 50 nm lower than the outside surface after hydrothermal treatment. This result clearly supports the hypothesis that the region with subsurface damage is more reactive than the pristine surface and can be preferentially etched by water under hydrothermal conditions.

Figure 3. (a) Vickers indent prepared with 500 gf load in 40% relative humidity; (b) indent from (a) after hydrothermal treatment at 150 °C for 24 hours.

Vickers indentation can be used to create regions with residual stress; when a radial crack is formed, the region in front of the crack tip is under residual stress.[3,35,36] As shown in Figure 3a, radial cracks were normally formed on the SLS float glass after indenting with a 500

gf normal load in 40% relative humidity air. After the sample was hydrothermal treated at 150 °C for 24 hours, the length of the cracks was increased by 22%. For some indents, new cracks were also formed as shown in Figure 3b. Again, this result supports that the glass surface with residual stress around crack tips can be selectively etched by hydrothermal treatment.

3.2 Mechanical properties of hydrothermally-treated SLS glass surface

The elastic modulus and hardness of the glass surface before and after hydrothermal treatment were measured with nanoindentation and are summarized in Figure 4. The elastic modulus and hardness were calculated from force-displacement curves using the Oliver-Pharr model.[37] The analysis was performed with four different indentation depths: 50nm, 100nm, 150nm, and 200nm. Since a surface layer with a modified chemical structure is expected to form during the hydrothermal treatment, the Poisson's ratio of the modified layer cannot be determined accurately. Therefore, the reduced modulus is reported rather than elastic modulus. It should be noted that the modified layer formed by hydrothermal treatment is not like an external film with an abrupt interface with the bulk substrate, but rather is a gradient layer that gradually changes in chemical and physical properties from the surface to the bulk. For these reasons, the accurate determination of mechanical properties for the modified layer was difficult; however, the qualitative trend of modulus and hardness for the modified layer can still be analyzed.

Figure 4. (a) Hardness and (b) reduced modulus of the SLS glass surfaces before and after hydrothermal treatment determined from nanoindentation.

Figure 4a shows that the overall hardness decreases after the hydrothermal treatment. This indicates that the silicate network is altered due to the reaction with water in the surface region, which could result in a hydrated layer. The longer treatment makes the glass surface softer, which can be associated with the thickening of a modified layer. As shown in Figure 4b, the reduced modulus of the surface treated for 24 and 48 hours is slightly higher than the pristine glass surface, and the surface hydrothermal treated for 72 hours is similar to the pristine surface. This non-monotonic trend must be related to an artifact associated with the modulus calculation in nanoindentation. When a soft layer is present on top of the glass, the softer layer could pile up around the probe tip during the indentation. Then the actual contact area is hard to determine from the indentation curves and could be larger than the area estimated from contact depth based on Oliver-Pharr method. As a result, the contact area estimated by the Oliver-Pharr method could be smaller than the actual contact area, leading to an overestimation of the reduced modulus.[38] In such a case, as the ratio of the indentation depth over film thickness increases, the reduced modulus will increase, reach a maximum, and then decrease. The reduced modulus estimated by

the Oliver–Pharr method is smaller for the 72 hour sample than for the samples treated for 24 hours and 48 hours since a thicker modified layer is expected for SLS glass that has been hydrothermally treated for 72 hours and the ratio of the indentation depth over film thickness.[38]

Figure 5. Vickers indentation before and after hydrothermal treatment at 150 °C for 72 hours under 300 gf load conditions at 40% relative humidity. (a) Summary of Vickers hardness; (b) Optical image of Vickers indentation of SLS glass before hydrothermal treatment; (c) Optical image of Vickers indentation of SLS glass after hydrothermal treatment.

Resistance to the nucleation of a crack in glass is a desirable property. Vickers indentation was performed with 300 gf on the SLS glass surface before and after hydrothermal treatment. Figure 5a summarizes the Vickers hardness before and after hydrothermal treatment. It should be noted that the hardness obtained from Vickers indentation is smaller than that from nanoindentation. This is because the Berkovich tip used in nanoindentation has a smaller size and a different shape than the Vickers tip used in microindentation.[39] The student t-test suggests that the difference in Vickers hardness is not statistically significant with 95% confidence ($p = 0.39 > 0.05$), which indicates that the bulk mechanical properties do not change by the hydrothermal treatment. No cracks are observed on the samples that are hydrothermally treated at

150 °C for 72 hours (Figure 5c) while the pristine SLS glass (Figure 5b) shows radial cracks from the Vickers indenter corners. Based on the nanomechanical properties of the hydrothermally treated surface determined in Figure 4, the surface layer formed by hydrothermal treatment is softer than the bulk. Thus, the resistance to crack formation after hydrothermal treatment cannot not be due to the compressive stress as is observed in chemically strengthened glass surface through ion-exchange process.[40] Instead, it must be due to the formation of a softer layer with modified chemical structure on top of the glass. The effect of such a modified layer formed from the bulk glass itself on fracture toughness of the surface has not been fully understood. One possible explanation is that the formation of the silica-like surface layer can prevent or suppress crack opening or initiation. This speculation is based on the fact that silica glass has higher fracture toughness than SLS glass.[18] Another possible explanation could be the changes in the network connectivity in the modified surface layer based on the topological constraint theory.[41] It is conceivable that the overall topological constraint in hydrothermally-modified surface region of SLS glass is altered since the number of Na-NBO sites decreases and hydrous species are introduced.[42]

3.3 Mechanochemical wear of hydrothermally-treated SLS glass surface

Unlike the alcohol VPL which prevents wear of the surface, water adsorption from the surrounding gas phase can induce mechanochemical wear due to hydrolysis reactions facilitated by interfacial shear.[43–45] The mechanochemical wear behavior of SLS glass shows a very unique humidity dependence.[19,20] Unlike other glass surfaces that show more wear as humidity in the test environment increases, SLS glass shows a decrease in wear as humidity increases, especially in near-saturation humidity.[44] While exact mechanisms of such

resistance to mechanochemical wear at high humidity are not fully understood yet, it is believed to come from dynamic interactions between leachable Na^+ ions and the silicate network in the presence of water molecules.[18] XPS analysis indicates that sodium ions are almost completely depleted in the hydrothermal-treated SLS glass surface (see Supporting Information). Thus, if the hypothesis involving the leachable Na^+ ions is correct, it is expected that the resistance to mechanochemical wear at high humidity is reduced or lost for the hydrothermal-treated SLS glass surface.

Figure 6. Comparison of wear tracks formed after 400 sliding cycles in (a) 40% relative humidity (b) 90% relative humidity on the pristine sample, the sample treated at 150 °C for 24 hours in dry air, and the sample treated at 150 °C for 24 hours in steam. (c) Comparison of the wear volume. The p-values in the figures are from comparison between two cases: pristine vs. heat-only and heat-only vs. steam-treated for the 40% humidity case and pristine vs. heat-only for the 90% humidity case.

The cross sections of the wear tracks produced at 40% and 90% relative humidity conditions for SLS glass surfaces before hydrothermal treatment and after heat treated at 150 °C for 24 hours in dry air and in steam are compared in Figure 6. The heat treatment in dry air was conducted to rule out the effect of thermal annealing on the wear behavior of SLS glass. As shown in Figures 6a, the wear behavior of SLS glass at 40% relative humidity is

indistinguishable for the pristine, heat-treated, and hydrothermal-treated surfaces (the p-values from *t*-test are provided in Figure 6c). However, the wear depth and wear volume at 90% relative humidity are significantly increased after hydrothermal treatment, while both pristine and heat-only treated SLS glasses show very little wear (Figures 6b and 6c). In Figure 6b, small positive spikes on the substrate surfaces are physical wear debris of the counter surface deposited on the SLS surface.[19] The increase in wear volume at 90% relative humidity compared to the 40% relative humidity case is similar to the mechanochemical wear behaviors of other glasses without leachable sodium ions.[4,20] The results shown in Figure 6 clearly show that the resistance to mechanochemical wear at high humidity is a unique property for the SLS glass network containing leachable sodium ions; once sodium ions are depleted, the mechanochemical wear resistance effect is lost.

3.4 Subsurface structural changes upon vapor-phase hydrothermal reactions

It is generally known that during the hydrothermal treatment, molecular water can diffuse into the SLS glass and induce the hydrolysis of the silicate network at the bonding oxygen sites:

or the ion-exchange at the non-bonding oxygen (NBO) sites:[11,46,47]

While these reactions are slow at ambient conditions, they can be significantly accelerated at a temperature higher than 100 °C.[13,48–50] First, the diffusion of water penetrating into the glass

network is accelerated at elevated temperatures.[51] Second, the reactivity of water molecules is also higher. For example, the ionization constant of water (K_w) at 150 °C is approximately 2 orders of magnitude higher than the value at room temperature.[52,53] In other words, the equilibrium concentration of protons and hydroxides are 10 times higher than normal water at room temperature. And, their thermal energy is higher compared to the ambient condition. Thus, hydroxide ions can catalyze the hydrolysis reaction (Eq.1) and the protons and hydronium ions can facilitate the sodium leaching reaction (Eq. 2 and 3). These reactions can occur not only when glass is in contact with liquid water, but also when the glass surface is exposed to steam at high temperature and pressure. It is conceivable that such reactions would occur more readily at the defect sites with strained chemical bonds, which can explain selective etching of the ‘invisible’ wear track formed in the n-pentanol VPL condition (Figure 2) and the region with residual tensile stress in front of a crack tip (Figure 3).

Figure 7. (a) SR-IR spectra of SLS glass before and after hydrothermal treatment. The treatment conditions is at 150 °C for 24 hours, 48 hours and 72 hours; (b) ATR-IR spectra of SLS glass before and after hydrothermal treatment for 12 hours at various temperatures; (c) Raw data and fitted curve for determining the activation energy of diffusion of water and formation of silanol groups into the glass network.

In order to understand the mechanical and mechanochemical property changes of SLS glass after hydrothermal treatment, analyses of the silicate network structure as well as the amount of and chemical environment of hydrous species (silanol groups and molecular water) were carried out. Figure 7a shows the SR-IR analysis on the changes of silicate network before and after hydrothermal treatment. As the reaction time between glass surface and water increases, the peak centered around 1056 cm^{-1} gradually shifts to 1064 cm^{-1} . In previous studies, this shift was normally observed at the surfaces where the density decreased due to the sodium depletion and the silicate network became a more silica-like structure.[54,55] These findings indicate that substantial reactions occur between water and glass surface during the hydrothermal treatment, modifying the subsurface silicate network structure.

The reactions between glass surface and water, and the diffusion of water molecules into the glass network, can be studied by examining hydrous species in the surface region before and after hydrothermal treatment. ATR-IR analysis was carried out to monitor the changes in the amount of these hydrous species in the subsurface of SLS glass. The information depth of ATR-IR is about $0.5\text{-}0.7\text{ }\mu\text{m}$ for the stretching vibration region of hydroxyl groups and $\sim 1.1\text{ }\mu\text{m}$ for the bending vibration region of molecular water.[56,57] As shown in Figure 7b, the molecular water peak at $\sim 1620\text{ cm}^{-1}$ grows as the hydrothermal treatment temperature increases. This provides direct evidence that water molecules diffuse into the glass network. The activation energy (E_a) for molecular water diffusion into the SLS glass can be obtained by assuming the Arrhenius relationship between the rate of diffusion (k) and temperature (T):

$$k = A \text{Exp}[-E_a/RT] \quad \text{Eq. 4}$$

where A is a pre-exponential factor. Since k is in a linear relationship with the amount of water molecules in the glass which is linearly proportional to the peak area (M) of the water bending vibration, k can be substituted with $b \times M$ where b is a constant. Then, equation (4) can be expressed as follows:

$$\ln(M) = -\frac{E_a}{R} \frac{1}{T} - \ln\left(\frac{b}{A}\right) \quad \text{Eq. 5}$$

By fitting the experimental data (Figure 7c) with a linear relationship in equation (4), E_a for diffusion of molecular water is calculated to be 40 ± 2.8 kJ/mol.

In the OH stretch region of mid-IR spectra of glasses, both silanol (Si-OH) and molecular water (H₂O) are detected. The small peak at ~ 3740 cm⁻¹ is assigned to free OH of molecular water without hydrogen bonding with surrounding molecules.[58,59] Although not well-resolved, the steep rise and shoulder in the ~ 3650 cm⁻¹ region suggests the presence of a distinctive OH component; when it is deconvoluted through peak fitting, the ~ 3650 cm⁻¹ component is generally assigned to free Si-OH without hydrogen-bonding with surrounding oxygen atoms.[60] All other components contributing to the broad feature from 3600 cm⁻¹ and 2600 cm⁻¹ can be assigned to OH groups (of both Si-OH and H₂O) with varying degrees of hydrogen bonding interactions.[61,62] In previous literature, the broad OH stretch peaks were fitted with an arbitrary number of components and varying peak widths and the component near 3400 cm⁻¹ was attributed to the molecular water in the glass network.[60,63,64] But, it should be noted that the deconvolution of the hydrogen-bonded OH stretch peaks cannot be done through such a simple curve fitting procedure. The OH peak position and width are complicated functions of hydrogen bonding strengths and dynamics.[65] For that reason, we did not attempt to deconvolute the broad OH stretch peak (Figure 7b).

It is noted that the Arrhenius plot of the OH stretching peak from 2600 cm^{-1} to 3800 cm^{-1} show 40.6 ± 1.2 kJ/mol (Figure 7c), which is the same as the molecular water diffusion. This implies that the production of the Si-OH species is either limited or controlled by the diffusion of molecular water (H_2O) or the transport rate of proton or hydronium ions ($\text{H}^+/\text{H}_3\text{O}^+$) is similar to the diffusion of molecular water. The former would accelerate the hydrolysis reaction (Eq.1) and the latter would accelerate the reaction of ion-exchange with sodium ions (Eqs. 2 and 3).

The E_a value determined for diffusion in SLS glass under vapor phase hydrothermal conditions is lower than the activation energy determined for pure silica glass. The E_a for water diffusion in the pure silica glass was reported to be ~ 70 kJ/mol by Wiederhorn *et al* and Zouine *et al* in the same temperature range and saturated vapor pressure.[22,66] For reactions between water and silica glass at 400 $^{\circ}\text{C}$ - 1000 $^{\circ}\text{C}$, the activation energy for water penetration into the glass and formation of Si-OH was found to be ~ 83 kJ/mol or higher.[67] It should be noted that during the reaction between water and silica glass in their studies, Si-OH is formed as a reaction product from the hydrolysis reaction.

The lower activation energy determined for SLS glass must be related to its alkali content and silicate network. Leaching of Na^+ in SLS glass has been proven to assist the water diffusion into its silica network.[57] The ion-exchange between Na^+ and hydronium ions results in the formation of Si-OH from NBO sites and molecular water in the glass network. The silicate network of SLS glass is also quite different from the silica network of pure silica glass. Based on molecular dynamics (MD) simulations, Tilocca *et al* suggested that the addition of modifiers like Na^+ can change the ring size distribution in the Si-O-Si network, which can create more open pathways for water molecules to move inside the glass.[68] MD simulations also suggest that water will preferentially interact with the Na^+ -NBO site over the BO site at the surface to allow

water molecules to penetrate into the glass.[69] Thus, the low E_a value implies a reaction-assisted penetration of water molecules into the SLS glass network and formation of Si-OH. Pure silica glass does not have leachable monovalent ions like Na^+ , which makes it thermodynamically difficult for molecular water to diffuse into the glass network and form Si-OH groups.

The changes in the silicate network and increase in the amount of hydrous species in the surface region of SLS glass after hydrothermal treatment can explain the lower hardness of the surface layer (Figure 4). The hydrated silica-like layer with the lower hardness could suppress crack opening during the Vickers indentation test (Figure 5b). Based on the hypothesis involving the leachable sodium ions, the loss of mechanochemical wear resistance at high relative humidity can be explained by the depletion of sodium ions and the modification of the subsurface silicate network after hydrothermal treatments (Figure 6).

Figure 8. SFG spectra of SLS glass before and after hydrothermal treatment at 150 °C for 24 hours, 48 hours and 72 hours respectively.

SFG is very sensitive to chemical environments of the hydrous species (Si-OH and H₂O) arranged noncentrosymmetrically at the surface and in the subsurface region of SLS glass.[54,70] The SO₂ dealcalization process of the manufactured float glass produces the subsurface hydrous species arranged or oriented noncentrosymmetrically which can be selectively detected with SFG as multiple sharp peaks in the OH stretch region.[70] Figure 8 shows the effect of hydrothermal treatment on these hydrous species in a 1mm thick SLS float glass. Before hydrothermal treatment, this SLS float glass shows five OH peaks at ~3180 cm⁻¹, ~3392 cm⁻¹, ~3552 cm⁻¹, ~3728 cm⁻¹, and ~3920 cm⁻¹. These SFG peaks represent hydrous species in the subsurface of SLS glass rather than physisorbed water molecules on top of the glass.[58,70,71] SFG intensities depend on the noncentrosymmetrically-ordered species in a complex manner; so, the accurate quantification of the detected species is difficult. Instead, the most useful information can be deduced from the peak positions and relative intensities of the detected OH vibrations.[54,70]

The peak at ~3728 cm⁻¹ must be the free OH groups without hydrogen bonding interactions with surrounding oxygen species.[59] The peak above 3800 cm⁻¹ is proposed to originate from the hydrous species (probably OH group) within the strained Si-O-Si network.[70,72–75] These strained sites in the silicate network would be more reactive than normal sites with bond distances and angles close to the equilibrium values; thus, they are expected to react more readily with water during the hydrothermal treatment, which would result in the selective disappearance of this peak after the hydrothermal treatment.

The peaks at $<3650\text{ cm}^{-1}$ are the hydrous groups with varying degrees of hydrogen bonding interactions.[61,76,77] In Figure 8, the SFG peak at $\sim 3392\text{ cm}^{-1}$ is increasing compared to other peaks; similarly, the ATR-IR spectra in Figure 7b show the largest increase at $\sim 3400\text{ cm}^{-1}$. The OH stretch peak position can be correlated with the O-H...O distance using the empirical relationship found from minerals.[61][70] Using the empirical relationship found in the literature,[61][70] the component near 3400 cm^{-1} could be attributed to the hydrous species with hydrogen bonding interactions with the O-H...O distance of $\sim 0.28\text{ nm}$. This value is very close to the equilibrium distance between two oxygen atoms connected via hydrogen bonds in liquid water;[78,79] but this does not assure that the only species contributing to the 3400 cm^{-1} peak is molecular water. Not only the OH stretch peak position of molecular water,[58,80] but also the OH stretch peak of the silanol group, vary over the same spectral range depending on the hydrogen bonding strength or distance.

With this spectral interpretation, we note that the distribution of the SFG OH peak intensities (Figure 8) is shifted to the lower wavenumber side, implying the growth of populations of hydrous species with shorter O-H...O distances ($3400\text{ cm}^{-1} = 0.28\text{ nm}$ and $3250\text{ cm}^{-1} = 0.27\text{ nm}$).[61][70] This finding might provide an explanation for the loss of mechanochemical wear resistance. Density functional theory (DFT) calculations reported that at the transition state of the proton-catalyzed hydrolysis of the Si-O-Si linkage, the distance between the oxygen of a hydronium ion and the BO atom is about 0.25 nm .[81]

One potential effect of the shear force exerted by the counter-surface during the wear test could be the distortion of the silicate network of SLS glass at the sliding interface, so that the distance between the hydrous species and the BO is reduced further toward 0.25 nm . If so, the hydrolysis reaction could be facilitated during the interfacial shear. If the hydrous species with

short O-H...O distances are highly populated at the sliding interface, the transition state for hydrolysis could be reached with a small distortion of the silicate network. This hypothesis could be one possible explanation for the increased wear of the hydrothermal-treated surface at high humidity (Figure 6). Further details of this mechanochemical reaction mechanism could be revealed through computation studies such as molecular dynamics simulations with reactive force fields.

4. Conclusions

The surface of SLS float glass was probed and modified by hydrothermal treatment in steam which involved penetration and diffusion of water molecules, hydrolysis reaction of bridging oxygen, and ion-exchange between Na^+ and hydronium ions/protons. It was found that hydrothermal treatment at $>150^\circ\text{C}$ can be used to reveal the subsurface damage of SLS glass since the area with subsurface damage or residual stress is preferentially hydrolyzed during the hydrothermal treatment. Hydrothermal treatment also creates a highly-hydrated silica-like layer with very little sodium. While the hardness of this modified surface layer is smaller than that of the bulk, the overall indentation fracture toughness of the glass surface increases. The hydrothermally-treated surfaces, unlike pristine SLS glass, become more susceptible to mechanochemical wear at high humidity. A hypothesis explaining the mechanochemical reactions leading to wear is proposed.

Acknowledgements. This work was supported by the National Science Foundation (grant No. DMR-1207328). The authors acknowledge Asahi Glass Inc. for providing the samples for this study.

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