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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.

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

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same wear resistant behavior at high humidity [19,20]. In aluminosicliate 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 the liquid phase.

2. Experimental details

SLS float glass with a 1 mm 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% SiO_2, 13.3% Na_2O, 7.7% CaO, 1.9% Al_2O_3, 4.4% MgO, 0.3% K_2O, and 0.1% Fe_2O_3 from X-ray fluorescence (XRF). During the manufacturing process, SO_2 treatment was applied after the glass was lifted from the tin bath onto the rollers, and this dealkalized 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 Fig. 1. It was performed in a sealed stainless steel vessel with a volume of 100 cm^3. 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 cm × 2 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].

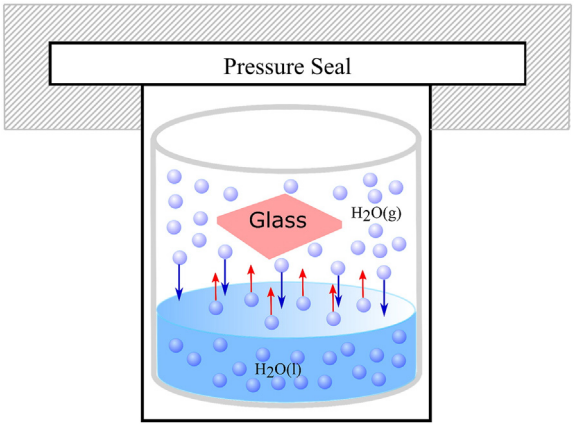

Fig. 1. Schematic representation of vapor-phase hydrothermal treatment of SLS glass at temperatures higher than 100 °C.

Specular reflectance infrared (SR-IR) spectroscopy was carried out with a Bruker Hyperion 3000 Microscope (Bruker, Co.) with a 15× 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 532 nm 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 AlKα (1486.6 eV) X-ray source was used. Survey scans of O 1 s, Na KLL, Ca 2p, Mg KLL, C1 s, Si 2p peaks and high-resolution narrow binding energy of O 1 s and C1 s 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 nanoindenation measurements was performed with displacement control. The maximum penetration depth was held at 50 nm, 100 nm, 150 nm and 200 nm for 2 s. The loading and unloading rate were both 20 nm/s. The results are averaged from >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 s. The Vickers hardness was averaged from >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,