Chemical toughening of glass by potassium diffusion: how non-bridging oxygen and a surface calcium barrier limit the process

Noboru TAKAMURE¹, David Robert McKENZIE¹, Marcela Maria Malena BILEK¹ and Alexey KONDYURIN¹

¹The University of Sydney School of Physics, NSW 2006 Australia

Chemical toughening of soda-lime glass by in-diffusion of potassium from a molten salt to replace sodium is currently restricted to applications where thermal tempering is not suitable, such as toughening of thin glass and complex shaped objects. Chemical toughening would be more attractive as a commercial process if it could be made more rapid by elevating the temperature, accelerating the diffusion process. However, when the temperature is increased, stress generation processes are accompanied by stress relief through structural relaxation, limiting the stress achieved. Here we use cross sectional microscopy with energy dispersive X-ray spectroscopy analysis and a study of the vibrational spectrum using Fourier transform infrared to show that there is another effect that also plays a role in determining the in-diffusion rate of potassium. Temperatures that initiate stress relaxation also accelerate the formation of excessive amounts of non-bridging oxygen which is accompanied by an increase in the surface concentration of calcium. We hypothesize that this calcium layer creates a barrier to the migration of potassium into the glass.

Key-words: Glass, Chemical toughening, Mixed Alkali Effect, Calcium, NBO

1. Introduction

The toughening of glass by thermally driven diffusion of ions into the surface has some key advantages over the more commonly used thermal tempering process. While both processes induce a compressively stressed surface layer that creates the toughening effect, chemical diffusion can be used to toughen thinner glass and to toughen glass objects of complex shape. Silicate glass has a siloxane chain structure which consists of linked SiO₄ tetrahedra. In addition, glass contains various positive alkali ions that act as modifiers. Modifiers are stabilized in the silicate host by combining with a Non-Bridging Oxygen (NBO) atom. The NBO atoms have a negative charge, attracting and stabilizing the positive alkali ion modifier. The number and type of modifiers impart physical characteristics to the silicate glass. Sodium and calcium are widely used as modifiers, producing the common type of glass known as soda-lime silicate glass.¹

Soda-lime silicate glass requires a toughening process for many applications such as safety glass panels and other architectural applications that require fracture resistance.

In a chemical toughening process for soda-lime glass, the sodium ions are replaced by the larger atomic diameter potassium ions, leading to an increase of surface compressive stress.² This stress increase can protect the surface from scratching which creates defects that initiates fracture under the Griffith law criterion.³

The Fick’s law diffusion coefficient of potassium in glass is temperature activated according to the Arrhenius Eq. (1) giving a diffusion rate constant that depends on time and temperature according to:

\[ k = A \exp \left( \frac{-E_a}{k_B T} \right) \]  

\( k \) is the diffusion rate constant, \( A \) is an attempt frequency factor, \( E_a \) is the activation energy, \( k_B \) is the Boltzmann constant and \( T \) is temperature. In a chemical toughening process, higher temperature is preferred because it enables potassium diffusion to proceed more rapidly to shorten the toughening process time with consequent economic advantages.

During the chemical toughening process, the glass surface may also undergo a competing stress reduction process caused by a thermally assisted creep of the glass that is assisted by higher temperature and longer process time.²,⁴,⁵ In order to obtain the best toughening process,
an optimum balance between the diffusion induced stress generation and the thermally assisted stress relief process must be found. Divalent positive ions such a calcium show a so-called mixed-alkali effect in silicate glasses. Divalent calcium ions combine with two NBOs, creating a strong bond that impedes the diffusion of monovalent ions like potassium, however, the detailed cause of this effect is still unclear. Because of this effect, calcium is added to soda-lime silicate glass to stabilize the glass against excessive sodium ion migration, but higher calcium concentration could potentially impede the inward diffusion of potassium ions, pointing to the need to manage the calcium concentration in a chemical toughening process. It has been noted that the presence of a small amount of calcium in a molten bath disturbs potassium diffusion strongly. In this study, we aim to determine the conditions of temperature and time that enable an optimization of the chemical toughening process by a detailed study of the diffusion of the three important ions in the process, namely sodium, potassium and calcium and the manner in which their interactions affect the stress generation and relaxation processes.

2. Experimental

2.1 Sample preparation

Soda-lime silicate glass samples 1.9mm thick were cut to 50 mm × 30 mm and cleaned with detergent and ethanol. Potassium nitrate, KNO₃, purchased from Sigma-Aldrich, Inc. was placed on the samples and melted to cover the surface by heating in an oven (B.& L.Tetlow Melbourne Australia). Annealing temperatures were 450, 500, 550°C and the annealing time was in the range from 1 to 50 h. After the annealing process, KNO₃ was removed from the glass surface by dissolving in water and the samples were dried.

2.2 Measurement and analysis

An optical stress meter, SCALP® (GlasStress Ltd.) was used for relative surface stress measurements. SCALP® observes the stress induced birefringence of the glass at a wavelength of 635 nm using a laser beam. Immersion oil of refractive index 1.52 was used to minimize surface reflectance of incident laser light. A refractive index value of 1.52 was set as the refractive index of the glass samples initially.

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The value for stress determined by the SCALP meter depends on the assumed stress distribution with depth. As the appropriate stress distribution for these measurements is not known, we used SCALP stress meter to obtain a relative measure of stress and calibrated the value against a curvature measurement of a thin soda-lime sample toughened on one side. The value was converted to a stress value using the Stoney Eq. (2).

\[
\sigma = \frac{ED^2}{3(1-v)tR}
\]  

\(E\) is the Young’s modulus (80.1 GPa), \(v\) is the Poisson’s ratio (0.27), \(D\) is substrate thickness, \(t\) is film thickness and \(R\) is radius of curvature change. The film thickness was measured by scanning electron microscopy (SEM).

Fourier Transform InfraRed Attenuated Total Reflection (FTIR ATR) was used to observe the molecular vibrations near the surface of the glass samples with a Digilab FTS 7000 Spectrometer using a Ge crystal ATR accessory from Harrick Inc. USA. FTIR ATR is sensitive to absorptions at depths of approximately on the order of 10 μm and has been used for silicate glass surface evaluations. The spectra were recorded with a spectral resolution of 4 cm⁻¹, for 500 scans. The spectral lines were fitted with Gaussians using Resolution pro® software.

A Phenom XL® (Phenom-World B.V.) scanning electron microscope was used for element profiling as a function of depth. Phenom XL® has an Energy Dispersive X-ray Spectroscopy (EDS) capability. In this experiment, the SEM was operated at 15 kV. For depth profiling, glass samples were fractured by propagating cracks from a scratch. Measurement points were integrated for 0.5 s at 512 locations.

X-ray Photoelectron Spectroscopy (XPS) (SPECS) was used for surface element analysis. AlKα X-rays irradiated the sample surface. An electron flood gun was used to compensate for the static charge build up in the sample during measurement. Force 500 Ellipsoidal crystal monochromators and a Phoibos 150 MCD-9 analyzer with 9 channels were used to record the spectrum over 50-1200 eV. CASA XPS software was used for analysis and compared with the literature.

3. Results

3.1 Stress

Figure 1 shows the stress in the glass samples as a function of annealing time in the presence of potassium nitrate as a molten film on the surface. The glass samples initially had low compressive stress. After baking at a temperature of 450°C, the compressive stress increased steeply with increasing baking time to 15 h then increased slowly until 50 h. This process at 450°C was used to produce samples of chemically toughened glass for subsequent experiments.

![Figure 1](image-url)  

**Fig. 1.** Stress as a function of annealing time at 450°C (blue circles), 500°C (orange squares) and 550°C (red diamonds) in the presence of potassium nitrate on the surface of soda-lime glass.
Baking at 500°C resulted in an increase in compressive stress up to 15 h and then a decrease to almost zero at longer times. Baking at 550°C produces a small increase in the compressive stress at short times but after 2 h the compressive stress decreases and tensile stress appears. In soda-lime glass, the ”annealing point” is said to occur at 450°C where stresses relax within a few minutes, according to Nordberg et al.\textsuperscript{2}

3.2 FTIR peak changes

The FTIR ATR spectra (Fig. 2) of soda-lime glass show three peaks in the range 1000–1100 cm\(^{-1}\) which we attribute to Si–O vibrations of silicate structures denoted as Cage, Network and Suboxide configurations.\textsuperscript{18} These Si–O peaks are also found in fused silica and have been attributed to structures with various Si–O bond angles.\textsuperscript{19} Literature values for these absorption peaks in silicon oxide thin films are shown in Table 1.

Figure 3 shows the spectrum of fused silica fitted with separate peaks attributed to the Cage, Network and Suboxide structures. The FTIR ATR spectra (Fig. 4) of soda-lime float glass show the same peaks with an additional shoulder at 963.5 cm\(^{-1}\), attributed to a non-bridging oxygen Si–O–Na vibration (Table 2).\textsuperscript{20,21}

The spectrum of the sample annealed for 25 h at 450°C with KNO\(_3\) shows that the low wavenumber shoulder has a higher intensity (Fig. 5). The fitting of this spectrum requires two NBO peaks in the shoulder, one at 963.5 cm\(^{-1}\) attributed to Si–O–Na vibrations and the second peak at 935.2 cm\(^{-1}\) attributed to Si–O–K vibrations.

![Fig. 2. Schematics of the Si–O–Si structures of silica and silicate glasses.](image)

**Table 1.** Si–O peak positions and corresponding Si–O–Si bond angles in thin film CVD silicon oxide with dielectric constant in the range \(k = 2.05\) to 2.8\textsuperscript{18}

| Name     | Peak position (cm\(^{-1}\)) | Si–O–Si angle (°) |
|----------|-----------------------------|-------------------|
| Cage     | 1135–1140                   | ~150              |
| Network  | 1063–1035                   | ~144              |
| Suboxide | 1023–1035                   | <144              |

![Fig. 3. The FTIR ATR spectrum of fused silica (blue) with fitted Gaussian peaks (orange, indigo, gray), the total fitted spectrum is green, corresponding to vibrations of the three SiOSi configurations of Table 1.](image)

**Table 2.** The peak positions of Si–O vibrations in FTIR ATR spectra of fused silica, as received float glass, float glass annealed at 450°C for 25 h and at 550°C for 5 h in the presence of KNO\(_3\).

| Peak position (cm\(^{-1}\)) | Cage     | Network  | Suboxide | Si–O–Na | Si–O–K |
|-----------------------------|----------|----------|----------|---------|--------|
| Fused silica                | 1150 ± 90.8 | 1070 ± 40.0 | 1025 ± 27.5 | —       | —      |
| No annealing                | 1150 ± 74.9 | 1070 ± 60.6 | 1025 ± 43.7 | 963.5 ± 55.9 | —      |
| 450°C 25 h                  | 1150 ± 74.9 | 1070 ± 60.6 | 1025 ± 43.7 | 966.8 ± 63.1 | 935.2 ± 22.5 |
| 500°C 5 h                   | 1150 ± 74.9 | 1070 ± 60.6 | 1025 ± 43.7 | 965.5 ± 68.2 | 935.9 ± 26.2 |
| 550°C 5 h                   | 1150 ± 74.9 | 1070 ± 60.6 | 1025 ± 43.7 | 946.4 ± 71.7 | 921.3 ± 29.2 |

![Fig. 4. The FTIR ATR spectrum of a float glass sample as supplied (blue), with fitted Gaussian peaks at the Si–O positions in fused silica for the Cage (orange), Network (indigo) and Suboxide (grey). The yellow line is the fitted SiONa vibration and the green line (overlapping the blue line) is the fitted total spectrum.](image)

![Fig. 5. The FTIR ATR spectrum (blue) of a float glass sample annealed for 25 h at 450°C in contact with KNO\(_3\). The orange line is the peak for the cage structure, the indigo line is for the network structure, the gray line is the suboxide structure, the yellow line is Si–O–Na, the red line is Si–O–K and the green line is the sum of all fitted peaks.](image)
position of Si–O peak in Si–O–Na and Si–O–K structures in a soda-lime glass can vary as a result of the various possible combinations of the NBO groups.

An alkali ion can be linked to a silicon atom via oxygen in 4 different configurations, depending on the number of NBOs at the silicon atom (Fig. 6). A “Q” notation is used to indicate for each structure the number of NBOs.13 Q⁰ indicates all four Si bonds are to a bridging oxygen while Q⁴ indicates all four Si bonds are to a NBO and so on. In alkali-silicate glasses, configurations Q¹ to Q⁴ are possible. In the presence of two alkali ions, Q² has three possible configurations in potassium diffused soda-lime glass, one is where both cations are Na, denoted NBO-Na, one where both are potassium, denoted NBO-K, and one is for mixed cations, denoted NBO-Na, K. The position of the Si–O peak is sensitive to the configuration. However, the difference in peak positions for different Q configurations is less than the width of the peak so that detailed fitting of the Si–O–Na and Si–O–K peaks, with different peaks corresponding to different Q values, is not reliable. The change in the distribution of local environments across the various Q values for different samples was therefore allowed for by flexible positioning of the Si–O–Na and Si–O–K peaks.

The spectrum of a sample annealed for 5 h at 550°C with KNO₃ is shown in Fig. 7. The Si–O–K peak is observed at 921.3 cm⁻¹. The SiONa peak is shifted from 963.5 to 946.4 cm⁻¹ through 965.5 cm⁻¹ for 5 h at 500°C sample (Fig. 8). The shift to lower frequencies for both these peaks shows that the sample annealed at 550°C has a different distribution of Q values than the sample annealed at 450°C. The integrated intensities of Si–O vibration peaks in the FRIR ATR spectra which are used in this paper is listed in Table 3.

**Figure 9** shows the Si–O–K peak position and area fraction of the total absorption for potassium diffused samples with annealing times of 450, 500 and 550°C.
to 15% during annealing. However, the spectrum of the sample annealed for 15 h at 550°C shows a decrease in the Si–O–K area fraction.

The depth profile of alkali ions of as received soda-lime glass shows a uniform distribution of the Na and Ca with depth (up to 60 μm) from the surface (Fig. 10). The profile of the sample annealed at 450°C for 25 h shows a decrease in the concentration of sodium ions and an increase in a concentration of potassium ions near the surface (Fig. 11). Profile changes are observed up to a depth of 30 μm. The calcium profile does not change under these conditions. The total amount of sodium and potassium remains constant along the depth. It indicates that the profile changes are due to an ion exchange process between sodium and potassium. The integrity of the surface layer is observed in the SEM image of the sample cross-section.

The depth profiles of samples annealed at 500°C show a disturbance of the calcium profile near the surface. (Fig. 12). After annealing for 50 h, the element profile shows a decrease in sodium concentration near the surface. The depth profiles of samples annealed at 550°C show the same features as for 500°C, except the changes take place much more rapidly. (Fig. 13) At the same time, the concentration of potassium increases. After annealing for 4 h the decrease in sodium concentration at the surfaces and the increase of potassium are evident. Further annealing for 20 and 50 h changes the profile significantly. The potassium concentration does not increase much but shows less noise in the profile up to depth of 60 μm. The sodium concentration decreases at a depth of 60 μm, but the concentration has a sharp peak near the surface. The calcium concentration shows a sharp increase near the surface and a decrease between 2 and 6 μm depths. Subsequent annealing of the sample for 50 h makes these changes more visible. The peak in sodium concentration near the surface becomes sharper and higher. The
positive and negative changes of the calcium concentration become more obvious. The SEM image of the cross-section of the sample shows a peeled off surface layer, appearing lighter in the SEM image consistent with a lower density. The surface of the sample took on a ‘milky’ appearance to the eye.

The XPS spectra (see Table 4) show an increase in the potassium concentration near the surface for the samples annealed at 450°C for 25 h. For a sample annealed at 500°C for 50 h the surface concentration of potassium has decreased despite the higher temperature and longer time. Simultaneously, the calcium concentration has increased. For samples annealed at 550°C, the time variation of the surface concentration is studied in detail. For 1 h annealing surface potassium increases as expected. Subsequent annealing at 550°C causes the potassium concentration to decrease to zero. The concentration of sodium and calcium increases for all annealed samples compared with the as received sample. The low concentration of these elements in the as received sample is attributed to surface contamination, evident in the relatively high intensity of the carbon peak.

The total concentration of NBO on the surface, calculated from a total positive electric charge of sodium (+1), potassium (+1) and calcium (+2) which combines to negative single charge of NBO (−1). Because the number of NBOs corresponds to the number of positive electric charges. The number of NBO remains constant for the samples annealed at 450 and 550°C for a short time. However, the NBO concentration increases significantly for the samples annealed for 20 and 50 h at 550°C.

4. Discussion

The aim of a glass toughening process is to generate stress in the surface layer of the glass without generating adverse effects. The adverse effects may include chemical changes that affect the chemical resistance and solubility, or optical changes that cause undesirable cosmetic effects. The results of this study provide the microstructural reasons for limiting the temperature and baking time in a chemical toughening process for soda-lime glass immersed in molten potassium nitrate. Our results show an effective limit of 450°C for the baking temperature because of changes in the Si–O bonding configuration. If a baking temperature of 500°C is used for times up to 5 h, an increase is observed in the contribution of the Cage Si–O structure relative to the Suboxide structure. This situation is reversed for baking at 550°C which causes a sharp decrease in the Cage to Suboxide ratio. These changes, beginning at 500°C, are correlated with changes in the alkali-NBO bonding at the surface. At 500°C there is a small increase in the NBO mainly due to the increase in potassium, while at 550°C there is a large increase in the sodium associated NBO.

Stress relaxation begins to limit the compressive stress achieved from a baking temperature of 500°C. There is an interesting correlation of the extent of NBO atoms in the structure and the relaxation of the stress. At 500°C for long baking times of more than 50 h, the presence of an increased sodium concentration on the surface is apparent which points to increased NBO at the surface. At 550°C, the strong increase in surface NBO associated with the high level of surface sodium is likely to encourage the out diffusion of calcium and its accumulation on the surface. These conditions are associated with the complete loss of surface compressive stress and the appearance of surface tensile stress, which is very damaging for the fracture resistance of the glass. EDS cross sectional analysis shows that after 20 h at 550°C there is a very large concentration of calcium on the immediate surface and a very large concentration of sodium just beneath the calcium rich layer. These conditions are associated with the roughness of the surface that spoils the appearance to the eye and is unacceptable from a cosmetic point of view. These observations suggest that there are two mechanisms for compres-
sive stress relaxation: one is purely thermal and allows the stress to be relaxed by movement of the glass without change in its composition; the other is chemical and is associated with major increases in the concentration of NBO atoms that ultimately leads to tensile stress.

Since calcium is known to inhibit the diffusion of the alkali cations, the presence of surface calcium will also act as a barrier to any further admission of potassium. The potassium that was already incorporated diffuses deeply but has a small concentration everywhere. In view of all of these changes, we recommend carrying out the toughening process at 450°C. The baking temperature of 450°C coincides with the maximum stress generation without serious structural impacts on the glass and is therefore the preferred baking temperature.

5. Conclusion

For successful chemical toughening of soda-lime float glass by baking in contact with potassium nitrate, it is necessary to achieve a high concentration of potassium ions by diffusion to a substantial depth while preventing thermally induced stress relaxation. In this study, we have shown that baking at 450°C for 50 h achieves the best result of all the conditions examined. If shorter processing times are attempted by increasing the temperature to 500°C, more rapid diffusion of potassium occurs, but the final stress level actually achieved is compromised by thermally induced stress relief so that the end result is lower stress even though greater depths of potassium diffusion may arise. At 550°C, potassium diffusion is achieved to a greater depth but is accompanied by rapid and serious stress relaxation together with major structural changes in the glass Si–O backbone. The amount of potassium that can enter subsequently is limited by the high surface concentration of calcium that we propose acts as a barrier to the diffusion of potassium, while creating other adverse effects such as a rough surface and possible surface failure. The calcium rich layer on the surface does not disperse with long baking times up to 50 h, indicating its stability on the surface. The knowledge gained from this study is useful to guide the design of chemical toughening processes.

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