

Mechanical strength improvement of a soda-lime–silica glass by thermal treatment under flowing gas

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Abstract

The incidence of thermal treatments in air, N₂ or NH₃, on the mechanical properties of a soda-lime silica glass is presented. The effects of the treatment time and temperature were studied. Ammonia treatments lead to the most important compositional changes near the surface: SIMS and XPS techniques revealed a significant depletion in alkali and alkaline earth cations and a limited incorporation of nitrogen. IR-reflexion spectroscopy provided evidence for compositional changes near the surface, from a typical soda-lime glass towards a silica glass composition. The affected surface layer is typically about 1 μm deep and leads to significant changes of the local mechanical properties. Nanoindentation measurements showed that hardness increases whereas Young's modulus decreases both by ~10% in a 300 nm thick surface layer. A significant increase of the indentation fracture toughness (K_{IC}) from 0.72 to 0.89 MPa.m^{1/2} was also noticed. The different processes leading to the cationic migration and to the changes of the glass surface properties were discussed.

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1. Introduction

The technological importance of nitridation treatments has been long recognized. For instance, nitridation of silicon dioxide films by chemical vapour deposition (CVD) routes has been extensively studied in the past 20 years due to its great technological interest in semiconductor science.¹ In contrast to SiO₂, silicon nitride and silicon oxynitride films have excellent diffusion-limiting properties and therefore exhibit a protective action against corrosion and impurity diffusion.² Besides, nitridation treatments are commonly used in industry to improve the mechanical performance of

steels.³ However, few papers are devoted to the surface nitridation of silicate glasses.^{4–6}

In 1966, Mulfinger⁷ achieved high temperature nitridation of glass melts and showed that nitrogen solubility in silicate melts was physically and chemically practical. The analyses of the glass compositions led to the conclusion that NH₃ gas was better than N₂ gas in nitridation performance.

This paper describes the effects of ammonia treatments on the structure and on the mechanical properties of a commercial window glass as a function of the treatment time and temperature. Results are compared with those of identical treatments made under air or in nitrogen (N₂). This process was already successfully used to synthesize pure aluminium nitride (AlN) from alumina (Al₂O₃) powders near 1300 °C.⁸ In addition, some heat-treatments were conducted under ammonia on both borosilicate and silica glasses to study the influence of the composition on the chemical solubility of nitrogen.

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2. Experimental procedures

2.1. Preparation of glass samples

Three commercial glasses were studied: a standard window glass (PlaniluxTM, Saint-Gobain Glass Company) with a glass transition temperature $T_g = 562$ °C, a borosilicate glass (BorofloatTM, Schott Glass Company) with $T_g = 560$ °C and a silica glass (SilicaTM, Saint-Gobain Glass Company) with T_g near 1100 °C (glass transition temperatures obtained from differential scanning calorimetric measurement). Some physical properties as well as the compositions of the glasses are given in the Table 1. The as-received 4 mm thick sheets were cut into 10×20 mm rectangular specimens, which were placed on vitreous silica or graphite supports. This latter support was used for NH₃ or N₂ treatments to study the effect of cyanide ions CN⁻ formation on glass reactivity. Samples were then introduced via a water-cooled vitreous silica tube and placed at the middle of an electric furnace as shown schematically in Fig. 1. Treatments were achieved by flowing a gas through the silica tube. Note that float glasses show up with two different flat surfaces after the float process: a tin contact—and an atmosphere contact—surface. All the characterization reported in this work concern the side in contact with the atmosphere.

N₂ and NH₃ treatments were conducted with a gas flow rate of 25 dm³ h⁻¹. Air treatments were performed under atmospheric conditions. Ammonia treatments consisted of three steps: increase in temperature under nitrogen flow up to the target temperature, introduction of NH₃ and then slow cooling under nitrogen atmosphere. Specimens were naturally cooled by switching the furnace off (average cooling rate of 2 °C min⁻¹).

2.2. Surface analysis of treated glasses

X-ray photoelectron spectroscopy (XPS) is a suitable technique to study the chemical reactions occurring at and beneath the surface, up to few nanometers depth. An ultra-high vacuum < 10⁻⁶ Pa was used and samples were carefully preserved from any atmosphere contamination.

The compositional changes in the near surface of glass, up to several hundreds of nanometres depth, were investigated by secondary ion mass spectrometry tech-

Table 1
Density, glass transition temperature (from DSC) and compositions (in mol.%)

| (mol.%) | d | T_g (°C) | SiO ₂ | B ₂ O ₃ | Na ₂ O | CaO | MgO | Al ₂ O ₃ |
|--------------------|-----|------------|------------------|-------------------------------|-------------------|------|-----|--------------------------------|
| Soda-lime glass | 2.5 | 562 | 70.8 | / | 12.8 | 10.2 | 5.9 | 0.3 |
| Borosilicate glass | 2.3 | 560 | 83.2 | 11.3 | 4.1 | / | / | 1.4 |
| Silica glass | 2.2 | ~1100 | 99.6 | Traces + 30 ppm OH | | | | |

nique (SIMS). In fact, the SIMS technique allows for the erosion of the solid in a controlled manner to obtain information on the in-depth distribution of elements.

Infrared reflexion spectroscopy measurements were carried out using a FTIR Nicolet-Nexus spectrophotometer. Spectra were collected from 700 to 1400 cm⁻¹ at an interval of 1 cm⁻¹. Data were averaged over 256 scans. A gold mirror was used as a reference to correct the experimental results.

2.3. Mechanical characterization

Both microhardness (H) and fracture toughness (K_{Ic}) were measured by the indentation technique using a Matsuzawa MXT 70 Vickers indenter. Loads of 98.1 mN and 9.81 N were applied for 10 s to measure the micro-hardness and the indentation toughness respectively. The projected diagonal of the pyramidal indentation (2a) and the length of the median-radial cracks (2c) were measured immediately after indentation using an optical microscope with ×40 magnification. Note that with a load of 9.81 N, $c/a \approx 3.6$, so that the following equation established for the semi-elliptical radial-median crack system holds:^{9,10}

$$K_{Ic} = 0.016 \pm 0.004 \sqrt{\frac{E P}{H c^{3/2}}} \quad (1)$$

where a and c were measured with an optical microscope equipped with a LCD camera, P is the applied load, E is Young's modulus and H is Meyer's hardness, expressed as:

$$H = \frac{P}{2a^2} \quad (2)$$

Measurements were done with accuracies better than ±0.2 GPa and ±0.01 MPa.m^{1/2} for hardness and fracture toughness, respectively.

A nanoindentation apparatus (NanoXP, MTS) with a Berkovich indenter was used to characterize H and E in the near-surface region treated specimens. Continuous stiffness measurements were performed during the nanoindentation experiments.^{11,12}

Strength measurements were carried out using a Lloyd Lr 50 K apparatus. Two sets of soda-lime-silica glass specimens were cut into 4×4×25 mm³ rectangular

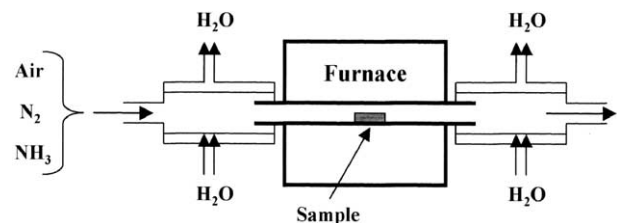


Fig. 1. Schematic drawing of the thermal equipment used for the heat-treatments.

bars and polished up to 9 μm with diamond spray. The first set was heat-treated under ammonia at $T=600\text{ }^\circ\text{C}$ for 1 week while the second set was annealed in air at $T=562\text{ }^\circ\text{C}$ for 1 h. Four-point bending experiments were performed with a crosshead speed of 0.1 mm min^{-1} until failure occurred. A Weibull distribution function¹³ was used to analyse the scatter of the strength data. The cumulative probability of failure for each fracture, P_i , was defined as: $P_i = (I-0.5)/N$, where N is the total number of specimens. The Weibull exponent, m , is obtained from the $\ln(-\ln(1-P_i))$ vs. $\ln(\sigma_R)$ plot. Considering the slope of the median fracture stress $\sigma_R(P_i=0.5)$ range, between $P_i=0.15$ and $P_i=0.85$, one gets:

$$m = \frac{2.46}{\ln\left[\frac{\sigma_R(P_i=0.85)}{\sigma_R(P_i=0.15)}\right]} \quad (3)$$

Twenty measurements were taken into account in the analysis.

3. Results

3.1. Mechanical characterization

3.1.1. Indentation

When indentation experiments were performed with a load of 98.1 mN, no change of the microhardness was noticed for NH_3 -treatment times shorter than few days. However, a slight increase of 7% was noticed after five days of nitridation at $560\text{ }^\circ\text{C}$. No changes were observed for higher applied loads. These preliminary measurements revealed the inadequacy of micro-indentation measurements to investigate the effects of the presently studied surface treatments on the mechanical properties. In contrast, nanoindentation experiments with normal load ranging between 0 and 100 mN (for penetration depth lower than 1 μm) gave evidence for significant changes of both hardness (H) and Young's modulus (E) in the near surface depth zone, i.e. between 50 and 500 nm (Fig. 2). Interestingly, the situation doesn't change much for treatment durations longer than 7 days. Furthermore, at depths larger than 500 nm under the surface, all curves tend asymptotically towards the characteristics of the untreated glass. Note that these latter values for E and H slightly differ from the ones of the bulk ones, as is mostly observed in nanoindentation measurements, since the derivation method is not fully self consistent yet.¹¹ Although not reported in Fig. 2 for the sake of clarity, decreases in Young's modulus and increases in hardness were also observed with N_2 , but the most spectacular effects are observed with ammonia in conjunction with a vitreous silica support.

The fracture toughness is a material intrinsic property and is therefore sensitive to composition changes. In our experiments, only near surface changes within few hundreds nanometers occurred, so that fracture toughness measurements from indentation crack lengths, which are typically 140–170 μm long for a load of 9.81 N (that is required to get a fully developed radial-median crack pattern) don't give the specific characteristics of the chemically affected layer, and are to be considered as apparent and somewhat averaged (over the depth of concern) values. The fracture toughness measured is therefore called apparent toughness. Fig. 3 shows the changes of the apparent toughness as a function of the NH_3 -treatment conditions. On one hand, a logarithmic-like increase of the crack propagation resistance is observed when the ammonia treatment time increases. On the other hand, an exponential improvement of the toughness is observed when the treatment temperature increases. This trend suggests a diffusion process: the reaction rate diminishes with time while the activity of gaseous species increases strongly with temperature.

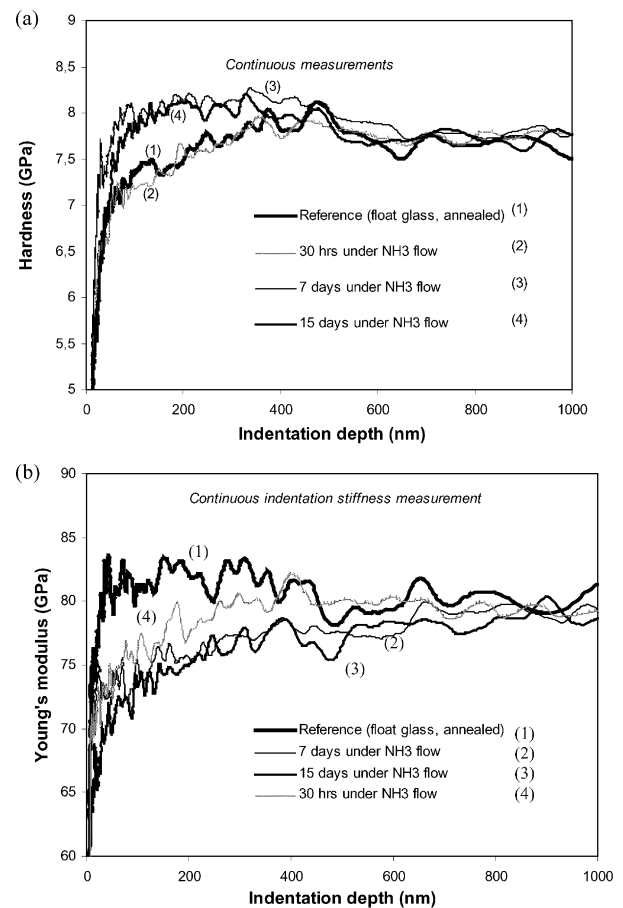


Fig. 2. Continuous indentation stiffness measurements on float glass specimens heat-treated under flowing ammonia for different duration: (a) hardness; (b) Young's modulus. Note that the results obtained after treatment in flowing N_2 at $600\text{ }^\circ\text{C}$ for 15 days almost follow the same trend and were not plotted for sake of clarity.

At a constant temperature (600 °C) for 65 h treatment time, the effect of the nature of the gas on the apparent toughness is given as follow: $K_c(\text{NH}_3) = 0.85 > K_c(\text{as-received}) = 0.76 > K_c(\text{N}_2) = 0.72 > K_c(\text{Air}) = 0.67$ MPa $\text{m}^{1/2}$. NH_3 enhances the crack propagation resistance whereas both air and nitrogen reduce the apparent toughness compared to the value measured for the as-received sample. In addition, the critical load for radial crack initiation, P^* , is higher after heat-treatment under flowing ammonia. In fact, at $P = 0.981$ N, no radial crack is observed in the case of treated samples whereas radial cracks propagate for a load as low as 0.5 N in the case of untreated samples (Fig. 4) and extend over 18 μm at 0.981 N. This observation illustrates the beneficial effect of the proposed treatment on both the initiation (P^*) and the propagation (K_c) of a radial crack during the indentation process.

3.1.2. Strength

The statistical distribution of the strength is plotted in Fig. 5. Note that the averaged failure stress (σ_R) increases, from 162 MPa for the annealed glass to 184 MPa for the glass treated for one week under ammonia. Weibull's modulus decreases from 8.3 to 6.5 when glass is heat-treated under ammonia. The scatter of the values after heat treatment suggests a non-uniform reaction between the gas and the glass surface. In fact, some

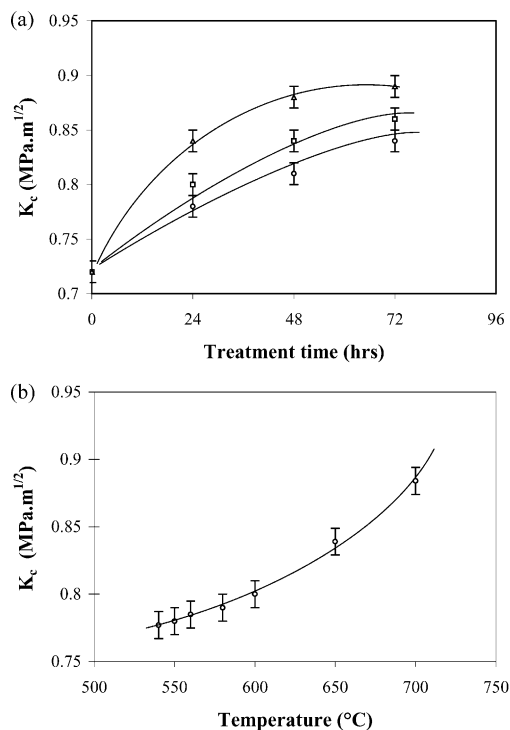


Fig. 3. Increase of the apparent toughness K_c (a) as a function of NH_3 -treatment time; (b) as a function of temperature for 24 h of NH_3 treatment. Error bars show the experimental error and mainly arose from the scatter on the crack length measurements.

bubbles appear when the temperature exceeds 650 °C. Bubbles seemed to be caused by some reduction processes. They appear as soon as the temperature of the glass reaches the T_g value (562 °C), i.e. when the viscosity of the glass becomes sufficiently low to allow for atomic movements over relatively large distances. Bubbles show up only with ammonia treatments and their occurrence at $T = 600$ °C could explain the scatter of the results for the set of ammonia-treated glasses. The generation of new surface flaws increases the scatter of the data, while the chemical reaction strengthens the surface.

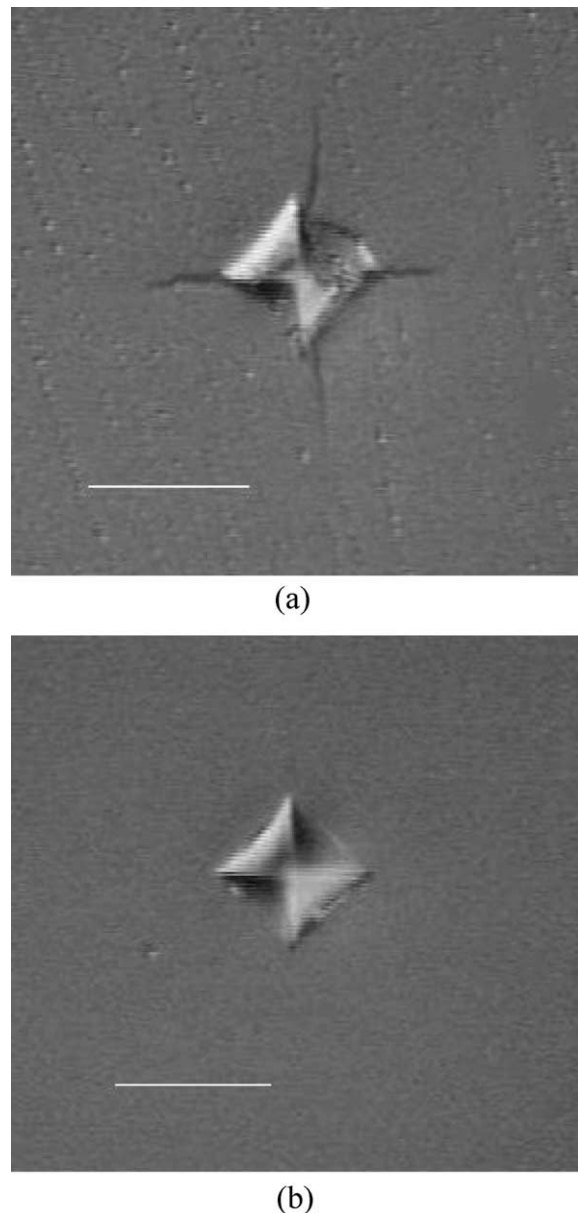


Fig. 4. Optical micrographs of indentations performed under 1 N in (a) the untreated annealed glass, and (b) after NH_3 treatment for 7 days at 600 °C. Bar = 25 μm .

3.2. Chemical and structural changes

3.2.1. Nitrogen incorporation

X-ray photoelectron spectroscopy (XPS) was first carried out in order to investigate nitrogen bonding into the near surface glass network up to five nanometers. The analysis after the heat-treatment at 600 °C for 1 week under flowing NH₃ reveals a low nitrogen content. The spectral integration of the N (1s) and O (1s) peaks gives a nitrogen content of about 1 anionic%. Other experiments were made on borosilicate and silica glasses both heat-treated for 1 week under flowing ammonia at 600 and 950 °C, respectively. These experiments were aimed to study the effect of the glass composition and of the temperature on the incorporation of nitrogen. XPS measurements indicate nitrogen contents of 1.2 and 1.4 atomic% for the borosilicate and the silica glasses respectively. Indeed, the amount of covalently bonded nitrogen is much improved when the modifier content decreases.

Two different depths, 4 and 5 nm, were analysed by setting the scanning angle at 60 and 0° (Fig. 6). Results regarding the energy of the extracted electrons reveal

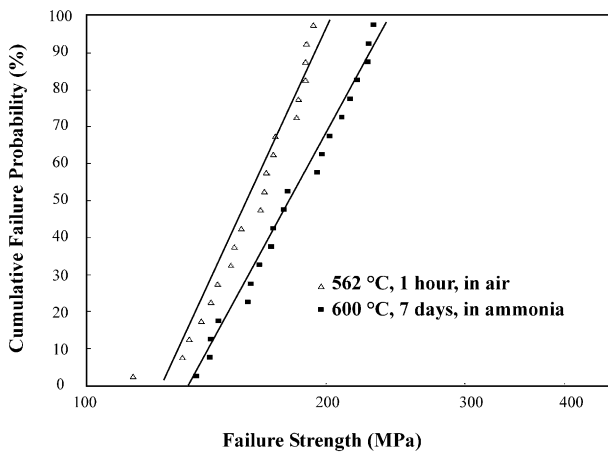


Fig. 5. Strength distribution for air-annealed float glass (562 °C—1 h) and ammonia heat-treated float glass (600 °C—7 days).

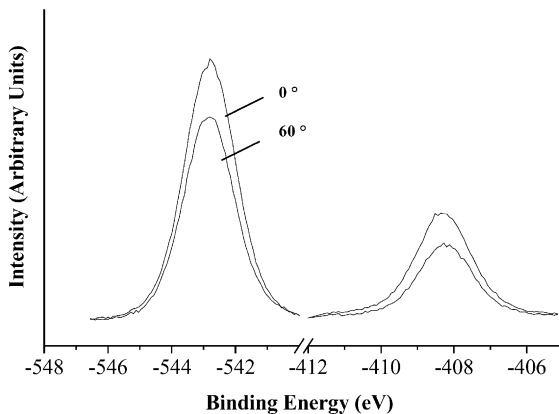


Fig. 6. Peaks position O1s (left) and N1s (right) photoelectron spectra measured for silica glass heat-treated at 950 °C for 1 week under flowing NH₃.

that nitrogen is covalently bonded to the glassy network. We can therefore conclude that the higher the modifier content is the smaller the quantity of the chemically added nitrogen is. This result is in good agreement with the fact that nitrogen tends to bond only with silicon and essentially replaces bridging oxygens.¹⁴ We can finally note that it is possible to make nitrogen enter the near surface of the silica network below its glass transition domain. In fact, a SIMS analysis of a heat-treated silica sample has shown that 2 atomic% of nitrogen was present in the near surface of glass, quantity which decreases linearly in the first 150 nanometers.

3.2.2. Alkali and alkaline earth depletion

In this part of the work, we have studied the effects of the nature of the gas (N₂ or NH₃), the type of support (silica or carbon graphite), the treatment duration (30 h, 7 days and 15 days) and the temperature (500, 550, 600 and 650 °C) on the migration process of the cationic species, for a standard soda-lime-silica glass. Changes in the cationic contents as a function of the depth were investigated by SIMS. Table 2 gives the composition of the soda-lime-silica glass (Planilux™).

Fig. 7 shows the effect of the treatment gas and support. The type of support has little influence on the cationic depletion using N₂ while this effect is more pronounced with NH₃ gas. NH₃ gas and a silica support is the most suitable combination for depleting the near surface of glasses. Note that whatever the gas used, the same composition is finally reached for the affected layer. Indeed, the gas seems to influence the depletion depth only.

Fig. 8 shows the maximum depletion obtained under NH₃ at T=600 °C after 15 days when the glass sample was set on a silica support. As can be seen, the glass

Table 2

Composition of the soda-lime-silica glass (Planilux, Saint-Gobain Co.)

| (cationic%) | Si ⁴⁺ | Na ⁺ | Ca ²⁺ | Mg ²⁺ | Al ³⁺ |
|-----------------|------------------|-----------------|------------------|------------------|------------------|
| Soda-lime glass | 62.5 | 22.7 | 9.0 | 5.2 | 0.6 |

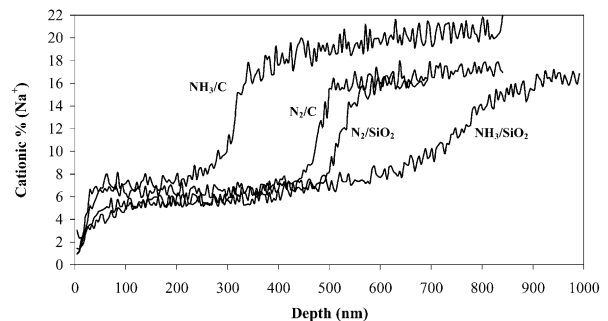


Fig. 7. Sodium depletion expressed in Na⁺ cat.% as a function of both gas and support used in thermal treatment during 15 days at 600 °C.

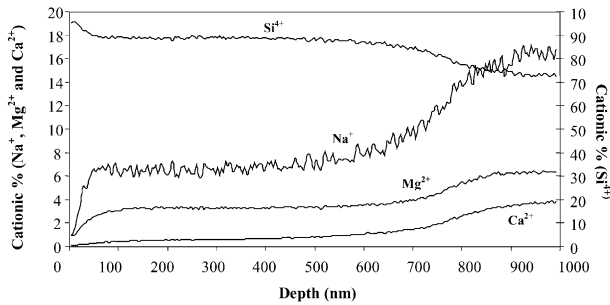


Fig. 8. Composition changes for a typical float glass after thermal treatment under NH_3 at 600°C for 15 days (silica support).

composition changed dramatically up to 700 nm beneath the surface. The silicon content reaches a value of 90 cat.%, whereas the percentages of sodium and alkaline earth are much smaller than before treatment. The calcium extraction is the most important phenomenon. Only 20 cat.% calcium is left in the affected layer. The sodium amount is divided by three while the magnesium one is half the initial value. Note that the com-

position is still affected 1 μm under the surface; the silicon content then reaches a 72 cat.% value while the calcium and the sodium contents are less than 4 and 17 cat.%, respectively. The depleted surface layer is about 600 nm thick (from 100 to 700 nm beneath the surface), and has been found to have a rather homogeneous composition.

Fig. 9 shows the influence of the treatment time on the glass composition. Note that the treatment time has little influence on the composition, although it changes the depth of the metallic cation depletion layer. The depth of the sodium depletion changes with the square root of the time, suggesting a diffusion process. This observation was made whatever the kind of cationic species (Na^+ , Mg^{2+} and Ca^{2+}) or the type of treatment (gas or support). Note that in all cases, magnesium is less depleted than calcium or sodium. Noteworthy, the depth of the affected layer correlates well with the depth over which E and H for the heat-treated specimens differ from the values for the reference glass, as observed by nanoindentation technique (Fig. 2).

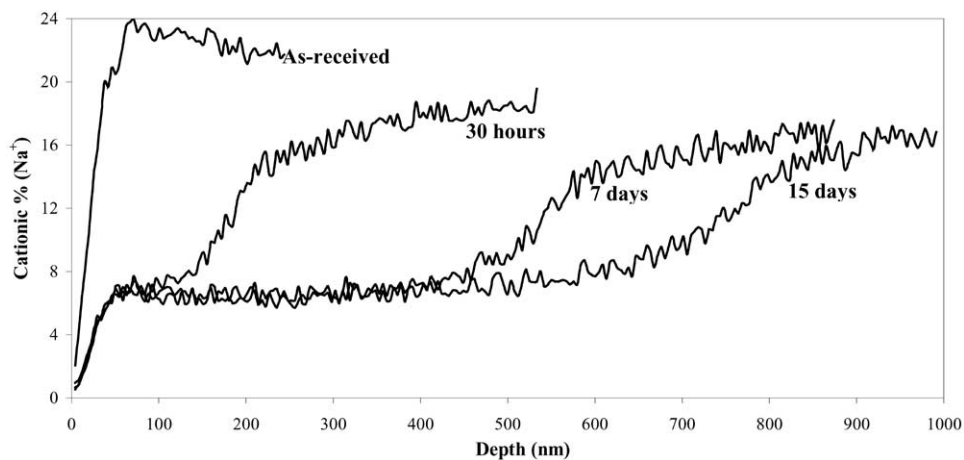


Fig. 9. Sodium (Na^+) depletion as a function of depth for different treatment times under NH_3 at 600°C compared with an as-received glass.

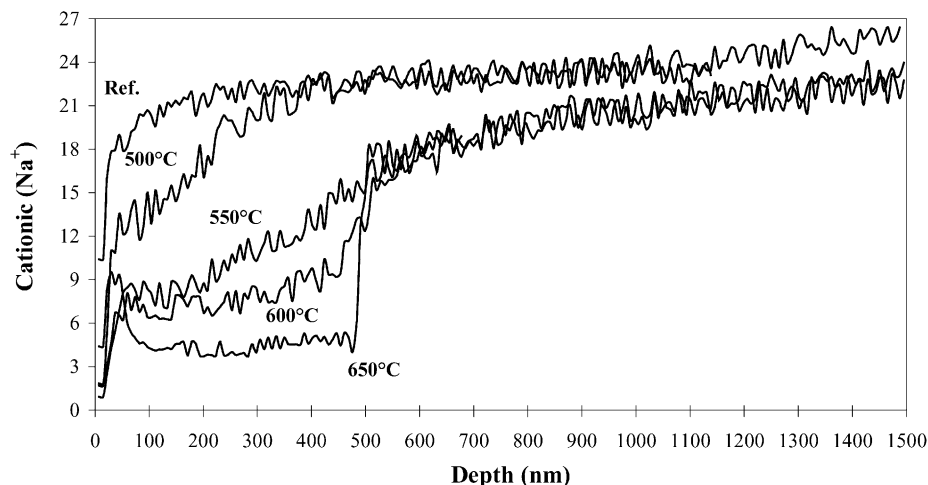


Fig. 10. Sodium (Na^+) depletion as a function of depth for different treatment temperatures under NH_3 for one week compared with an as-received glass.

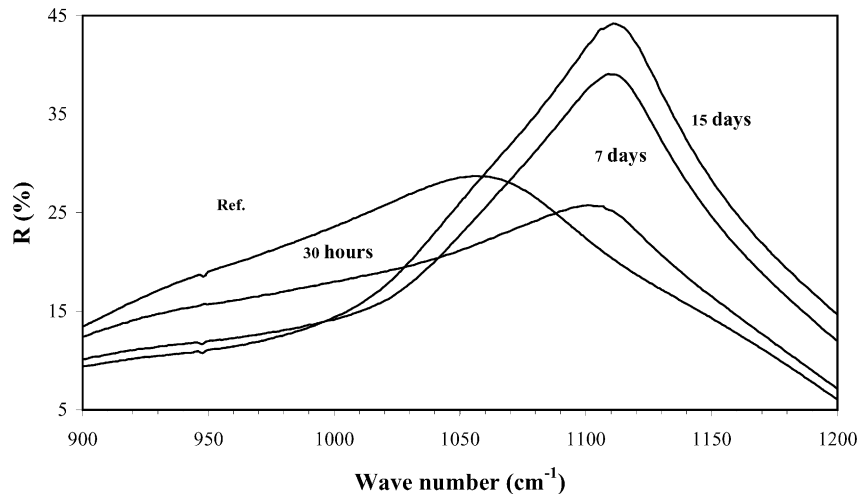


Fig. 11. Reflectance FTIR infra-red spectroscopy made on a soda-lime-silica heat-treated at 600 °C under flowing NH_3 (silica support) as a function of the time of treatment.

Fig. 10 shows the effect of the temperature of treatment for a one-week treatment made under flowing ammonia (silica support) on the sodium depletion. An increasing temperature raises both the depth of cationic depletion and the final composition. This observation stands for the different cationic species such as Na^+ , Mg^{2+} and Ca^{2+} . Note that a limit of diffusion seems to be reached at $T = 650$ °C for a depth of 500 nm.

The literature gives several peak assignments for silicate bonds. Four peaks were observed and previously discussed and assigned to silicate bonds:^{15,16} the first peak near 940 cm^{-1} is assigned to the Si–OH while the peak near 990 cm^{-1} is due to the Si–O– Na^+ groups vibration. The peak near 1050 cm^{-1} is commonly assigned to the Si–O–Si asymmetric stretching in a complex silicate glass while the 1120 cm^{-1} peak is assigned to the asymmetric stretching vibration of Si–O–Si bridges in silica glass. Fig. 11 illustrates the evolution of the infrared reflectance of the glass surface as a function of the treatment time, from 900 to 1200 cm^{-1} . The typical Si–O–Si asymmetric stretching wavenumber increases from 1056 to 1111 cm^{-1} when the treatment duration is raised. The evolution of the wavenumber shows that the composition of the glass tends to a high silica content glass, which confirms SIMS results. The increase in reflectivity is also in accordance with that result.

4. Discussion

4.1. Incidence of the treatments on the mechanical properties

4.1.1. Hardness and Young's modulus

Nitrogen is well known in alumino-silicate glass systems for its strengthening and tightening effect on the

vitreous network. Nitrogen increases the interconnectivity of the tetrahedral silicate chains whereas modifiers provide weak bonding pathways for crack propagation. In fact, many papers provide evidence for a raise of the glass transition temperature, viscosity, density, Young's modulus, hardness and toughness when nitrogen (trivalent) replaces oxygen (divalent) into the structure.¹⁷ Nevertheless, it seems that both the magnitude and the depth of nitridation process are too small in the present case to affect the mechanical properties. The cationic depletion is the most likely reason explaining the increase of the hardness and the decrease of Young's modulus. This later assumption is supported by the fact that the silica glass possesses a higher hardness value¹⁸ and a smaller (not much though) Young's modulus than a standard window glass.¹⁹ In fact, the near surface composition of the treated glasses tends to the one of a high silica content glass.

4.1.2. Improvement of the resistance against microcracking

The improvement of both the resistance to crack initiation (P^*) and propagation (K_{Ic}), when glass is heat-treated under ammonia, can be partially related to the diminution of the number of non-bridging oxygens. It is indeed assumed, following Greaves et al.²⁰ and Hand et al.,²¹ that non-bridging oxygens provide weak resistance pathways for crack propagation. However, the development of residual stresses upon cooling from the treatment temperature gives a major strengthening effect. In fact, the near surface containing less cationic modifiers than the bulk glass surely possesses a thermal expansion coefficient lower than that of the untreated bulk glass and may therefore experience compressive strain upon cooling. This may have a significant effect on the indentation crack length, as is discussed below. Note that the effect of the temperature seems to be more

pronounced than the one of the duration of treatment, and that the type of gas has a strong influence on the apparent toughness value. Ammonia is the most suitable gas to enhance the crack propagation resistance. The apparent toughening effect is probably underestimated since the investigated area is much deeper than the affected one, which according to SIMS and nanoindentation measurements is about 500 nm to 1 μm deep at maximum. For instance, with a 9.81 mN indentation load, the indentation depth is about 9 μm and the crack length is between 70 and 90 μm long (c). The compressive residual stresses existing in the surface layer and responsible for the observed increase of the microcracking resistance can be evaluated by means of two different ways: (i) From the effective indentation crack length (surface observation) assuming that the mechanical characteristics of the surface layer are the same as the ones of the untreated bulk glass, and (ii) From the thermal mismatch appearing upon cooling between the surface layer and the “substrate”. Following Lawn and Fuller,²² the residual stress caused by—and effective in—a thin layer of depth δ from the sample surface is expressed as:

$$\sigma_i = \frac{1 - c_o/c}{\sqrt{\pi\delta[2 - \sqrt{\delta/c}]} K_{Ic}} \quad (4)$$

where c_o and c are the radial/median crack lengths [Eq. (1)] before and after surface-treatment respectively and K_{Ic} is the fracture toughness of the untreated glass.

Neglecting the elastic-strain in the substrate and assuming plane stress conditions, the residual stress, which develops in the dealkalized layer upon cooling, is given by:

$$\sigma_{ii} = -E(\alpha_s - \alpha) \Delta T \quad (5)$$

where E and α are the Young's modulus and thermal expansion coefficient of the untreated glass and subscript s stands for the surface layer. ΔT is the temperature interval considered for the calculation. In a first approximation T_g is taken as the onset temperature for the development of residual stresses so that: $\Delta T \approx RT - T_g \approx -542$ °C (RT: Room temperature). Further considering a glass heat-treated for 7 days at 600 °C under NH_3 , the depleted layer thickness (δ) is close to 0.5 μm and its composition is close to (Si, Na, Mg, Ca, Al) = (87.9, 7.5, 3.2, 0.8, 0.6) in cation at.% (see Table 2 for comparison) so that following the composition-based relationship proposed by Lakatos et al.,²³ the thermal expansion coefficient of the layer is: $\alpha_s \approx 5.84 \cdot 10^{-6} \text{C}^{-1}$. With $E = 72$ GPa, $H = 5.3$ GPa, $\alpha = 9.3 \cdot 10^{-6} \text{C}^{-1}$ and $K_c = 0.72$ MPa $\sqrt{\text{m}}$, one obtains: $\sigma_i = -106$ MPa and $\sigma_{ii} = -135$ MPa. Note first that the above estimations are in remarkable agreement, suggesting that the thermal mismatch is the main con-

tributing factor in the present case. Moreover, it is likely that the residual stress value σ_{ii} be slightly overestimated due to the fact that the viscous stress relaxation was not taken into account. Also, σ_i may be underestimated since the resistance of the surface layer to indentation cracking (radial/median system) is probably higher than the one of the untreated glass as the composition get closer to the one of silica.

4.1.3. Strength

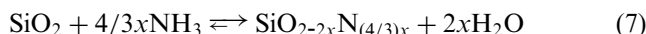
As can be seen in Fig. 4, heat-treatments lead to a slight improvement of the failure stress while the Weibull modulus decreases. This result shows that a new flaw population was generated during the treatment. The surface of a treated glass exhibits a higher roughness with in the extreme case (treatment at $T > 650$ °C for several days) the presence of microcavities. This observation can explain the scattering of the failure stress in the case of the ammonia-treated glass and so the decrease of the Weibull modulus.

4.2. Compositional changes

Only one anionic percent of nitrogen has been inserted into the near surface of the soda-lime-silica glass whereas, consistently to Ref. 6, 23 anionic% of nitrogen were introduced in the pure silica glass. After the cracking of the ammonia molecules,



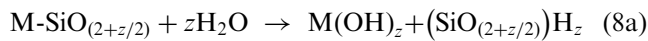
the nitridation process is explained by the reaction of nitrogen and hydrogen on the silica network to produce water⁴ so that the final reaction writes:



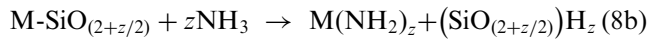
The SIMS analysis of the surface of the heat-treated silica glass showed that the hydrogen content does not increase. This indicates that water diffused out of the glass.

More interesting is the depletion of the modifier species when soda-lime-silica glass surface is heat-treated. It is observed that different treatment conditions (gas, support) lead to different depths while the same composition is obtained for the affected layer. This suggests that both the nature of the gas and of the support drive the process of cationic depletion.

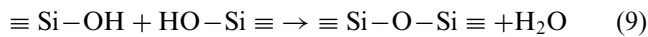
First, since nitrogen is a rather inert gas—and it was shown earlier²⁴ that a direct reaction between nitrogen and SiO_2 is not realistic—water is likely to be the reactive species. Both N_2 and NH_3 gases contain some water: nitrogen contains more than 10 ppm of water and ammonia more than 400 ppm of water. Water and ammonia may react with the glass to produce an exchange $\text{M}^{z+}/z\text{H}^+$, according to:



and/or



In these processes, hydroxide (8a) and/or amino (8b) compounds form at the glass surface and hydrogen leaves the glass bulk as part of water molecules by condensation of two neighbouring silanol groups (9):



The result is the progressive conversion of a soda-lime-silica glass network to a high silica content glass. Note that this process is rate-limited by the diffusion of the water molecule.

The second hypothesis considers the co-diffusion of cationic species with oxygen. This process may be enhanced when the temperature is near or above the glass transition temperature, i.e. for $T \approx 560$ °C. The way the oxide compounds leave the surface of the glass remains unspecified though. Further reaction with water could lead to the formation of hydroxide compounds, which could be volatilized. This scheme of reactivity is somewhat confirmed by the results in Fig. 10 which show a great improvement of the depth of cationic depletion layer when the treatment temperature is raised from 500 °C (below T_g) to 550 °C (near T_g).

As can be seen, the cationic depletion is a complex phenomenon, which may have different origins. Note that the presence of carbon graphite has a slight influence in the case of the N_2 -treatment but reduces greatly the depth of the cationic depletion when NH_3 is flowing. This could be explained by the formation of cyanide groups CN^- by reaction between nitrogen and carbon. The presence of carbon decreases the reactivity of the glass surface whatever the gas flowing through the silica tube. In the case of the nitrogen-treatment, the formation of cyanide groups could allow a similar depth of cationic depletion by increasing the ease of depletion via the formation of cyanide compounds M(CN)_z . Nevertheless, the above-discussed processes are valid or feasible if the cationic species are extracted from the glass. However, it is still unclear whether or not some of these units (M(OH)_z , $\text{M(NH}_2)_z$ or M(CN)_z) diffuse into the bulk of the specimens.²⁵ Results of SIMS gave evidence for a higher quantity of cationic species in the bulk after heat-treatment than in the as-received glass, between 1 and 2 μm . Further investigations are needed to get more insight into this phenomenon.

4.3. Time and temperature dependences of the cationic extraction

We have seen that the depth of cationic depletion increases with the square root of the time of treatment,

whatever the type of cationic specie and the kind of treatment. This suggests diffusion processes in all cases. The compositions of the heat-treated glass specimens tend towards an asymptotic limit, whatever the cation of concern and the treatment duration. This limited reaction can be explained by some structural considerations. In fact, nearly 80% of the calcium whereas only 40% of the magnesium moved from the surface when the treatment-temperature is 600 °C. It is known that calcium is bigger than magnesium and diffuses slower than the latest. Instead of that, we find that magnesium diffuses less than calcium. This observation leads us to think that magnesium and calcium are not iso-structural into the glassy network. Magnesium is known to enhance the tendency of glasses to form different sub-networks.²⁶ This difference of diffusion ability could mean that magnesium is partially present in some segregated parts of the network whereas the calcium is present in some conduction pathways.

Increasing the treatment-temperature improves the amount of cationic species depleted. A threshold in depth seems to be reached near 500 nm whatever the cationic species. Note that when the temperature is well above the T_g , for instance at 650 °C, the relatively low viscosity of the glass allows the cations to move more easily: 95% of the calcium, 80% of the sodium and 75% of the magnesium are extracted from the surface. Here again less magnesium species diffuse compared to the calcium, which has totally disappeared from the first 500 nm deep layer.

5. Conclusion

The effects of heat-treatments conducted under N_2 or NH_3 gas between 500 and 650 °C on different glasses and for different duration times were investigated. A little nitrogen is incorporated into the glass network but a strong cationic depletion was observed in the case of the soda-lime-silica glass. Compared with other processes of alkali depletion using SO_3 Ref. 25 or HCl gases,²⁷ our experiments lead to the extraction of both alkaline and alkaline earth species. Regarding the effects on the mechanical properties, the proposed treatments enhance the resistance of the glass to the initiation and the propagation of radial cracks during indentation while the hardness increases and Young's modulus decreases. These observations are consistent with FTIR spectroscopy results, which showed that the near surface of the glass evolved from the one of a standard window glass composition to the one of a high silica content glass. The cationic depletion was also experimentally followed by the SIMS technique. It was observed that both the time and the temperature have a beneficial effect on the depth and the amount of cations depleted from the surface. Further investigation is

required in order to better understand the way the cations are extracted from the surface and the role of water in this process.

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