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Effect of KNO₃ Molten Bath Na Enrichment on the Mechanical Performances of Ion-exchanged Soda-Lime-Silicate Glass

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http://dx.doi.org/10.5772/60976

Abstract

Systematic doping of pure molten KNO_3 bath by sodium nitride was used to analyze the effect of salt poisoning on the mechanical performances of chemically tempered soda-lime-silicate float glass. The ion-exchange process appears partially influenced by the presence of limited amount of Na in the potassium nitride bath. The interdiffusion coefficient and the penetration depth of K are invariant for $NaNO_3$ content up to 5 wt%; conversely, the surface concentration of potassium scales with the purity of the bath, and this accounts for different compressive residual stress. Nevertheless, the overall reinforcement associated to the final strength does not show clear dependence on the used bath mainly because of the large scatter in the surface flaws sizes, as typically observed in glass.

Keywords: Ion exchange, Chemical tempering, Sodium poisoning, Soda-lime-silicate glass

1. Introduction

The very first records of ion-exchange can be traced back to the Middle Ages, when glass artists used a mixture of silver salts, clay, and natural oil to obtain yellowish color in silicate glasses. The salts mixture was deposited on the glass surface and heated at about 600°C in reducing atmosphere, inducing the diffusion of silver ions into the glass and the formation of silver nanoparticles [1, 2]. Since then, the ion-exchange process was applied without much scientific

knowledge. It was in the 20th century that scientist started to understand the surface of chemically tempered glasses and figured out an exchange between monovalent cations in glasses with silver and/or potassium cations in the molten salts [2, 3]. These investigations increased the industrial application of the ion-exchange process, especially with the aim of enhancing the optical and mechanical properties of glass [4].

Glass strength can be largely increased by the ion-exchange process, otherwise called chemical tempering. The exchange of small ions such as Li^+ or Na^+ in an alkali-containing glass, with larger ions such as K^+ from a molten KNO_3 bath at temperatures below the strain point of the glass, is responsible for the creation of bi-axial residual compressive stress in the surface layers of the material. Because glass products generally break due to excessive tension applied at a surface flaw, the introduction of surface compression strengthens the glass component.

During the ion-exchange treatment, the glass matrix is considered as a solid negatively charged structure where some mobile ions (Na^+ in soda-lime-silicate glass) can be replaced by larger monovalent ions (K^+ from molten KNO_3) responsible for the generation of a compressive stress. The replacement takes place through an interdiffusion process, according to the Nernst–Planck equations. The flux of the ion species scales with the interdiffusion coefficient [2]:

$$\bar{D} = \frac{D_{Na}D_K}{D_{Na}N_{Na} + D_K N_K}$$

(1)

where N_i is the fractional concentration of alkali ion i (Na or K) and D_i the self-diffusion coefficient. One important parameter in the interdiffusion phenomenon is clearly the concentration of ions in the molten salt. Some studies have shown that the presence of poisoning elements (already present in the salt or coming out from the glass as in the case of Na) can hinder the diffusion of K^+ into the glass and slow down the exchange process, thus reducing the strengthening efficiency. An important issue in industrial practice is also the replacement/renewal of the molten salt which is time and money consuming [5]. Some researchers [3, 6], on the other hand, believe that the ion-exchange process is not affected in the presence of specific amount of poisoning elements.

In the present work, a systematic analysis of the effect of small amount of sodium as poisoning element in the molten bath on the performances of the strengthened soda-lime-silicate float glass was carried out.

2. Experimental procedure

Commercial soda-lime-silicate float glass sheets with nominal thickness of 4 mm were used. Table 1 summarizes the composition of the glass.

SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO
71	1	13	1	4	10

Table 1. Composition (wt%) of the float glass

The sheets, obtained from one single original plate, were cut into square samples of 50 mm × 50 mm. The edges of the specimens were rectified and polished with SiC abrasive paper. The samples were then rinsed and cleaned gently in water, avoiding any damage on the glass surface.

A semi-automatic chemical strengthening lab scale furnace was used for the ion-exchange treatment. In each run, 20 samples were placed in a stainless steel basket to be treated at 450 °C for 4 h, with 30 min preheating and 30 min post-cooling above the bath. At least 60 samples were treated in each bath with the same thermal and time conditions.

Pure KNO$_3$ and NaNO$_3$ salts from Sigma Aldrich were used. Pure potassium nitrate was systematically poisoned by adding a specific amount of NaNO$_3$ as reported in Table 2.

Added NaNO$_3$ (wt%)	0	0.1	0.2	0.5	1	2	5
Bathlable	A	B	C	D	E	F	G

Table 2. Amount of NaNO$_3$ added to pure KNO$_3$ in the considered salt baths

After each treatment, the samples were rinsed with water and carefully dried.

The surface residual stress and the case depth were optically measured by surface stress-meter (FSM-60LE, Luceo Co., Ltd., Japan). Bi-axial flexural test [7] was used to measure the strength. This was carried out with a ring-on-ring configuration with the upper loading ring and the lower support ring having a diameter of 8 mm and 40 mm, respectively. The actuator speed was $1\frac{mm}{min}$. The strength was determined from the maximum load (F) as:

$$\sigma_F = K\frac{F}{h^2} \tag{2}$$

where h is the thickness of sample and

$$K = \frac{3(1+v)}{2\pi}\left(\ln\frac{D_S}{D_L} + \frac{(1-v)(D_S^2 - D_L^2)}{0.72D^2(1+v)}\right) \tag{3}$$

where D_S and D_L are the radius of the upper and lower supporting ring, respectively, D the sample size (50 mm), and v the glass Poisson's ratio. A certain number of as-cut samples were also tested in this way for comparison.

Some fragments were collected from the broken samples and used for determining the potassium penetration profile. The fragments were attached on an aluminum disk by conductive adhesive tape and then coated by sputtering with Au-Pd alloy. Clean and flat portions of the fracture surface were analyzed in a Scanning Electron Microscope (SEM) (JSM5500, Jeol,

Japan) and the potassium Kα signal was recorded on a path of ~30 μm long by using the Energy Dispersion X-ray Spectroscopy (EDXS) (EDS2000, IXRF System, USA) probe. The chemical composition of the external surface of the glasses after the ion-exchange process was analyzed in the same way in a region of about 0.5 mm^2.

3. Results and discussion

The residual stress (σ_r) measured on the surface of glasses treated in the different molten salts is reported in Figure 1. The residual stress clearly decreases as NaNO$_3$ content increases, especially above 0.5%.
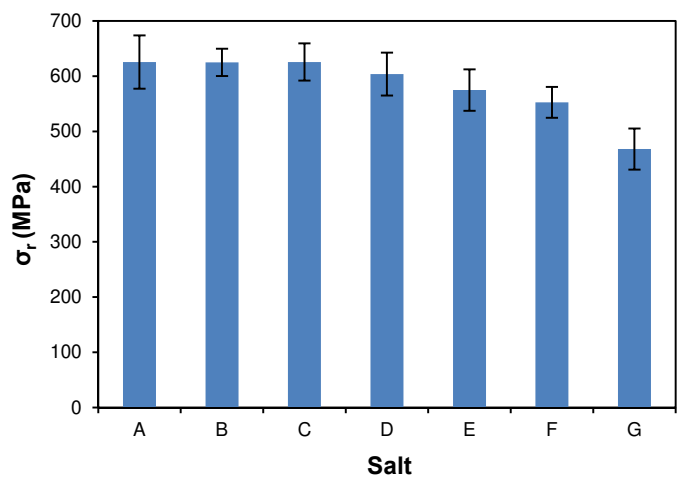
Figure 1. Compressive residual stress on the surface of glass ion exchanged in the different salt baths.

Conversely, the case depth reported in Figure 2 shows a quite different trend and actually seems almost invariant as a function of the sodium content of the salt bath.
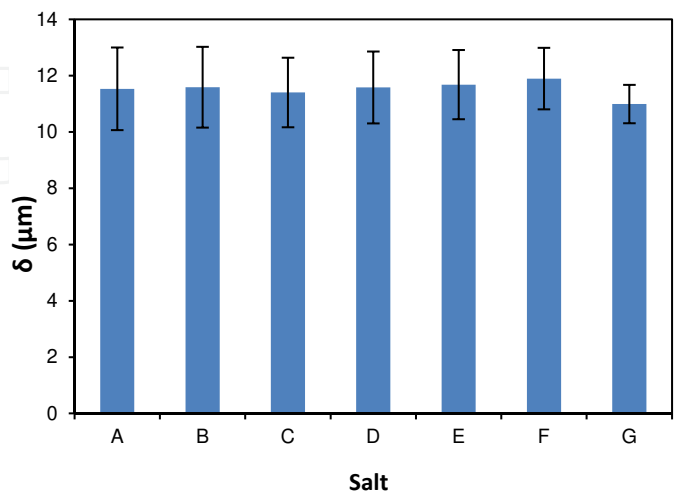

Figure 2. Case depth as a function of the exchanging bath.

The strength of ion-exchanged samples is shown in Figure 3. In spite of the typical large scatter and the relatively short duration of the ion-exchange process (compared to typical industrial duration, usually in excess of 8 h), the strengthening effect is clear in any used salt bath, and the failure stress increases by a factor of about 2.2–2.4 with respect to the as-cut glass. Nevertheless, the large strength scatter does not allow to point out specific trends with respect to the Na content of the exchanging baths.
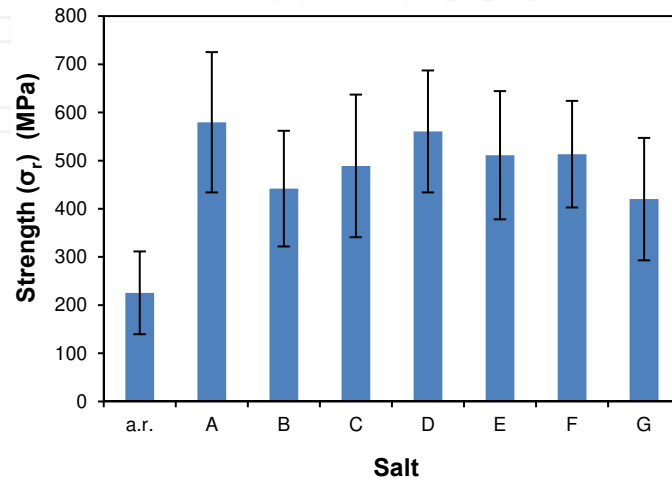

Figure 3. Average flexural strength as a function of the exchanging bath (the standard deviation is also shown).

A more effective representation of the strength data is possible by using Weibull plots where the measured strength data are reported as a function of failure probability. Here, failure probability was calculated as:

$$P = \frac{i - 0.3}{N + 0.4} \qquad (4)$$

where i is the rank in the ascending ordered strength distribution and N the total number of samples considered for each condition. The obtained Weibull plots are shown in Figure 4. One can easily observe again the evident strengthening effect in any salt bath with respect to as-cut samples; conversely, no specific trend can be seen with respect to the purity of the used bath.

The relationship between failure probability and tensile stress is typically expressed as:

$$P = 1 - \exp\left[-KS\left(\frac{\sigma}{\sigma_0}\right)^m\right] \qquad (5)$$

where S is the surface area of the sample under tensile stress, K the loading factor (whose units are per unit area), m the Weibull modulus, and σ_0 the normalizing stress, representing the

scatter of the distribution. Taking twice the natural logarithm of both sides, a linear equation can be obtained, which is functional for the Weibull modulus calculation [8]:

$$\ln\left(\ln\left(\frac{1}{1-P}\right)\right) = m\ln\sigma + \ln\frac{KS}{\sigma_0^m}$$
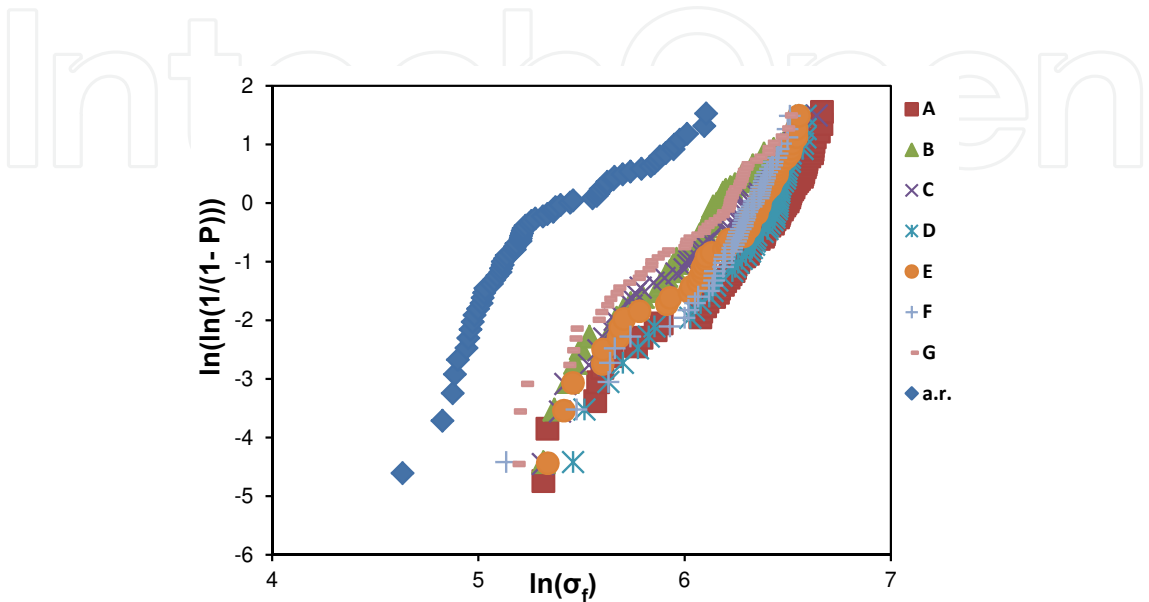
(6)

Figure 4. Weibull distributions for treated and untreated(a.r.) glasses.

Table 3 reports the Weibull modulus for the various distributions shown in Figure 4. One can observe that the moduli are also unaffected by changing the purity of the bath.

Salt	A	B	C	D	E	F	G	a.r.
Weibull modulus	3.9	4.1	3.6	4.4	3.9	4.4	3.5	3.2

Table 3. Weibull modulus of the strengthened glasses in different baths along with the as-received glass

The surface concentration of K$^+$ and Na$^+$ measured by EDXS is shown in Figure 5. There is a drastic increase in the potassium concentration after the ion-exchange process but the potassium concentration follows substantially the same trend of the surface residual stress (Figure 1), thus indicating a strict correlation between the amount of exchanged ions and the developed "stuffing"/reinforcing effect.

The potassium concentration profiles recorded by the EDXS line analysis always resembled a typical Nernst–Planck diffusion trend, which can be expressed as:

$$C_K'(x,t) = \frac{C_K(x,t)}{C_{K_0}} = erfc\left(\frac{x}{2\sqrt{\bar{D}t}}\right)$$

(7)

where x is the distance from the surface, t the ion exchange time, C_{K_0} the potassium concentration on the surface, and $\overline{D}$ the interdiffusion coefficient. The potassium concentration experimental data were fitted by Equation (7) to determine the interdiffusion coefficient and the penetration depth, identified as the distance from the surface where the potassium concentration is lower than 2% with respect to the surface one. Figures 6 and 7 show the obtained results.
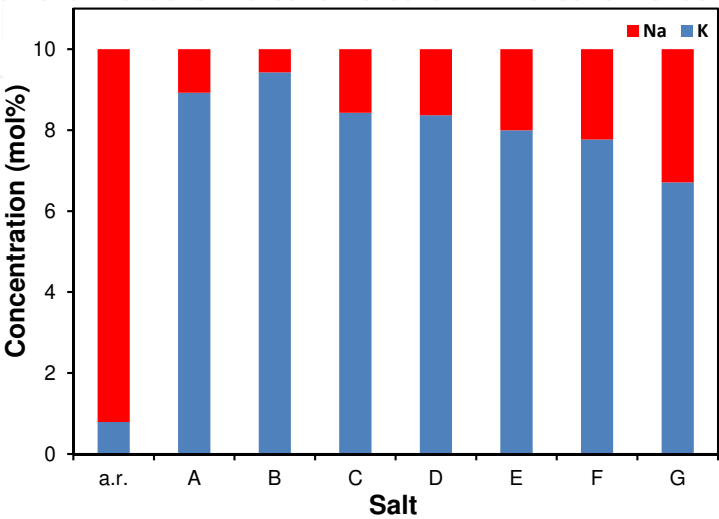

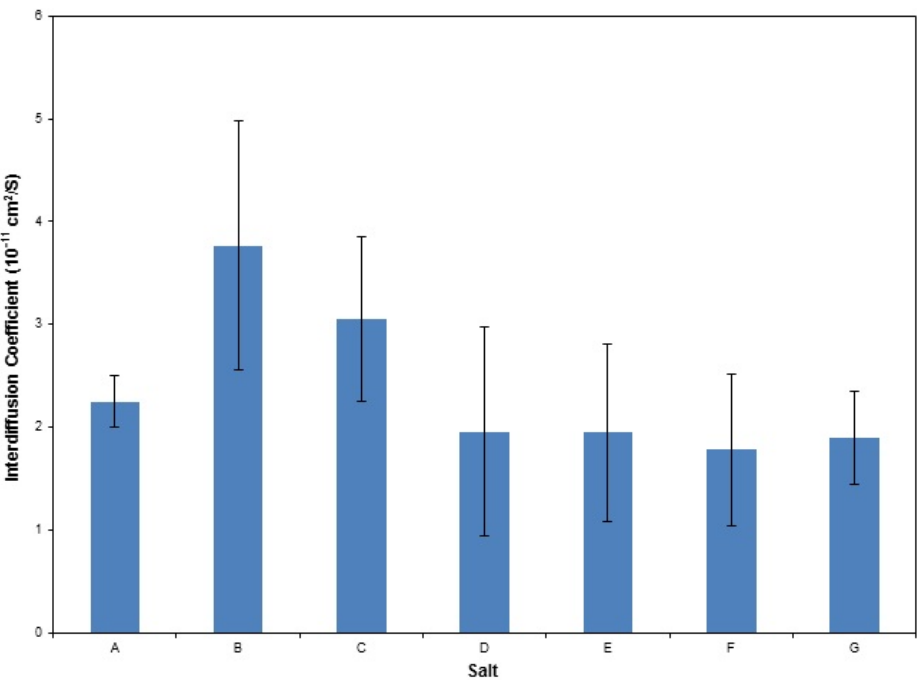**Figure 5.** Potassium and sodium concentration on the surface of treated and bare glass.

Figure 6. Interdiffusion coefficient for potassium in the different baths.
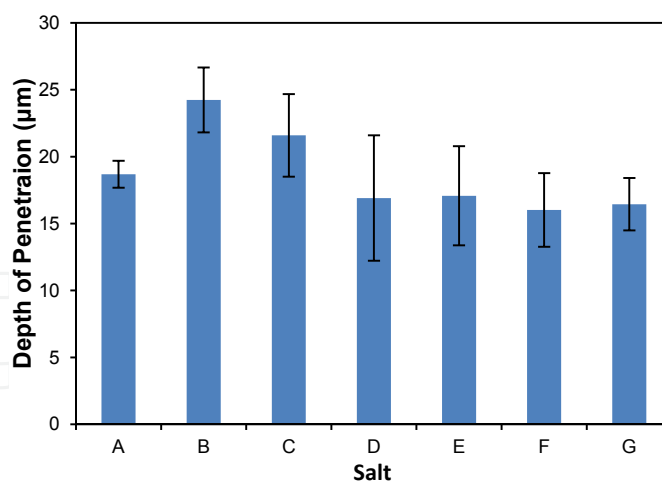
Figure 7. Depth of penetration for potassium during the ion-exchange process in the different baths.

The interdiffusion coefficients are in very good agreement with data reported in previous works [9, 10]. It is also confirmed that the $\overline{D}$ is not really affected by the presence of limited amounts of Na (up to 5%) in the KNO_3 bath [11]. Conversely, the surface concentration and, consequently, the concentration of potassium in the sub-surface layers are lower when the glass is treated in the Na-containing bath. On this basis, the K surface concentration in Equation (7) scales with the concentration in the used salt. Accordingly, the residual stress on the surface (shown in Figure 1) is higher when very pure KNO_3 bath is used, while the case depth does not change to an appreciable extent. Nevertheless, the effect of Na-containing salts on the final strength is substantially negligible, as shown in Figures 3 and 4. Clearly, this is mainly associated to the experimental scatter of the strength measurement, related to the typical dispersion on the surface defect sizes. In addition, due to the limited exchanging time used in the present work, some of the flaws are not "fully" reinforced; as a matter of fact, starting from the strength of the as-cut glass (ranging from ≈ 100 MPa to 400 MPa) and assuming, for simplicity, semicircular surface cracks, one can calculate that flaw sizes vary from ≈5 to ≈80 µm. Therefore, according to the case depth (Figure 2) and K penetration (Figure 7) results, it is evident that only a portion of the surface defects are completely "immersed" in the residual compressive stress field. Deeper defects, in a simplified model that considers flaws as invariant and perfectly closed during the ion-exchange process, are conversely subjected to a residual stress that changes from highly compressive on the surface to slightly tensile at a certain depth (below ≈12 µm). The effect of the initial flaw sizes, i.e. of the surface quality of the bare glass, appears to be more important in the ion-exchange process than the presence of limited amount of Na in the salt bath.

4. Conclusions

The presence of a small amount (up to 5 wt%) of $NaNO_3$ in potassium nitride bath partially influences the strengthening process of soda-lime-silicate glass when the treatment is carried

out over a duration of 4 h. The interdiffusion coefficient and the penetration of K in the glass are substantially invariant while the surface concentration of potassium scales with the purity of the bath, and this is responsible for different compressive residual stress, which is higher when pure KNO₃ is used. Nevertheless, the overall reinforcement associated to the final strength does not show clear dependence on the used bath mainly because of the large scatter in the surface flaws sizes, as typically observed in glass. It is clear that the quality of the surface of the bare glass in terms of flaws has a much higher importance than the salt purity in the final mechanical resistance.

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