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Influence of KNO₃ Bath Composition on Ion Exchange Process of Commercial Soda Lime Silicate Float Glass

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1. Introduction

Ion-exchange has been used exactly for one century to modify the surface properties of glass; Schülze in 1913 [1] was in fact the first to demonstrate that monovalent cations contained in glass could be exchanged when a soda lime silicate glass was immersed into a bath of molten silver nitrate. During the years, ion-exchange processes were developed and industrialized for numerous applications, such as chemical strengthening of glass articles [2, 3], gradient index (GRIN) lenses [4, 5] and planar waveguides [6]; the ion-exchange properties of glass have been also used to explain the functioning of the pH glass electrode and the chemical durability of glass [7].

In the last years, ion-exchange of glass has re-acquired great interest due to the possibility to increase the strength also of three-times and to work on articles of different shapes (even curved, wavy or hollow) and with limited thickness, avoiding many of the problems associated to thermal tempering such as optical distortions of the surface and premature failure due to NiS inclusions. Several contemporary technologies and applications, which regard the modern everyday life, took fundamental advantages from the application of ion-exchange to glass components such as pharmaceutical packaging, transparent lightweight armor, transparencies for private vehicles, trains and aircrafts, 3D / touch / flexible displays, photovoltaic modules [8].

Typically, an industrial ion-exchange process is performed by placing the glass components for several hours (from about 4 h even to 120 h) in a vessel containing a molten salt; in the most typical configuration sodium (or lithium) containing silicate glass is immersed into a molten potassium nitrate bath at temperatures ranging from 400°C to 500°C [9-11]. During the ion-exchange process the glass can be considered as a matrix of immobile negative

groups with associated mobile cations (Na$^+$ or Li$^+$); the contact with liquid monovalent ion-containing salt induces interdiffusion that can be treated with Nerst-Plank equations. After the ion-exchange process is completed, the articles are rinsed with water and dried, being immediately ready for successive use. For a given glass composition, the overall strengthening is a function of the type of invading ion (salt bath composition), bath temperature and immersion time.

In the past, no much attention has been devoted to the variation of chemical composition of the salt bath, to its influence on the ion-exchange process and resulting chemical, physical and mechanical performances. As a matter of fact, since interdiffusion depends on the concentration of the ions, one should expect that any variation in the liquid bath composition modifies the ion-exchange process. In addition, some recent results [12] pointed out a more effective ion-exchange process when the glass article is immersed in a non-pure liquid bath containing significant amount of the ion to be exchanged present in the glass.

There is therefore an increasing interest in the analysis and understanding of the influence of salt bath composition on ion-exchange process and consequent properties for silicate glasses.

In the present work soda lime silicate float glass from commercial source was considered and were subjected to ion-exchange in different KNO$_3$ salts. The treated samples are then characterized in terms of potassium penetration profile and mechanical strength to point out the influence of the bath composition on final performances.

2. Experimental procedure

Float soda lime silicate glass plates (nominal thickness = 4 mm) from commercial source was used in the present work. The composition of the glass is reported in Table 1. The glass transition temperature measured by Differential Scanning Calorimeter (DSC) (DSC2010, TA Instruments, USA) method [13] is equal to 577°C.

SiO$_2$	Al$_2$O$_3$	Na$_2$O	CaO	MgO	other
72	1	13	9	4	1

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

The original sheets were manually cut into 50 mm x 50 mm square plates whose edges were carefully rectified and polished by using SiC abrasive paper; care was also used to avoid any damage especially on the surface of the samples.

The samples were subjected to ion-exchange treatment by using a lab-scale furnace that allows the treatment of 19 small square plates contemporaneously. Three different potassium nitrate salt bath were used: (A) chemically pure (>99.9%) KNO$_3$ from commercial source, (B) pure (>99%) KNO$_3$ for industrial use from commercial source and (C) KNO$_3$ from different sources used for at least 1000 h in chemical strengthening process in the cited furnace.

The specimens were initially cleaned with water, gently swabbed and placed in the stainless steel holder. This latter was then positioned within the semi-automatic chemical strengthening furnace. The following conditions were used for the ion exchange process: pre-heating within the furnace above the salt bath surface = 20 min, duration of the ion exchange process = 4 h or 24 h, post cooling above the salt bath surface = 20 min, temperature of the salt bath = 450°C. At the end of each cycle the samples were carefully cleaned with water and gently swabbed before successive mechanical testing. At least 30 specimens were treated by using the same bath/time treatment condition.

Before starting the ion-exchange process the salts were subjected to chemical analysis. Small amounts (few grams) of salt were collected randomly from each solidified bath and dissolved in specific volumes of bi-distilled water; the obtained solutions were then analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) (Spectro-Ciros, Germany) and a multi-element standard (Sigma Aldrich) was used for the quantification of the dissolved ions. The melting point of the salts was also measured by DSC.

The ion-exchanged samples were then subjected to mechanical testing for the measurement of bi-axial flexural strength [14, 15]. Bi-axial flexure was carried out with a ring-on-ring configuration, the upper loading ring and lower support ring having a diameter of 20 mm and 40 mm, respectively. The tests were performed in lab air (temperature ≈ 22°C, relative humidity ≈ 40%) with an actuator speed of 1 mm/min. The failure stress was evaluated from the measurement of the maximum load, F_{max}, by using the following equation:

$$\sigma_F = K \, \frac{F_{max}}{t^2} \tag{1}$$

where t is the thickness of the sample and

$$K = \frac{3(1+\mu)}{2\,\pi}\left[\ln\frac{r_2}{r_1} + \frac{(1-\mu)}{(1+\mu)}\frac{\left(r_2^1 - r_1^2\right)}{0.72\,L^2}\right] \tag{2}$$

μ being the glass Poisson's ratio (equal to 0.2 [16]), L the specimen size (50 mm), r_1 and r_2 the upper and lower support ring radius, respectively. The tests were performed also on one set of as-cut glass plates for comparison.

Fragments of the samples subjected to mechanical testing were used to measure the potassium penetration profile in the surface layers on the fracture surface. The specimens were initially attached to an aluminum disk by using conducting adhesive tape and then coated by sputtering with Au-Pd alloy. Once placed within a Scanning Electro Microscope (SEM) (JSM5500, Jeol, Japan), clean and flat portions of the fracture surface were analyzed and the potassium Kα signal was recorded on specific paths (about 40 μm long) by using the Energy Dispersion X-ray Spectroscopy (EDXS) (EDS2000, IXRF System, USA) probe. By using a similar procedure, the chemical composition of the external surface of the glasses after the ion-exchange process was determined on clean regions of about 0.5 mm².

3. Results and discussion

The results of the mechanical tests are summarized in Table 2. One can observe the general increase of the mechanical resistance after the ion-exchange process although the scatter of the measurements does not allow to point out specific differences among the different treatments. There is anyway an increase in the average failure stress in excess to 60-70 MPa that is associated to the development of a compressive residual stress on the surface of the samples.

For a better understanding of the resistance data, strength values were analyzed by using the Weibull statistics. Figure 1 shows the failure stress distributions where the failure probability associated to each single measurement was calculated as:

$$F = \frac{j}{N+1} \tag{3}$$

where j is the rank in the ascending ordered strength distribution and N the total number of specimens. Failure probability is typically related to the tensile stress through the relationship:

$$F = 1 - \exp\left[k\, S \left(\frac{\sigma}{\sigma_0} \right)^m \right] \tag{4}$$

where S is the surface of the sample subjected to tension, k the loading factor, m the Weibull modulus and σ_0 the normalizing stress [17]: it is reminded here that the Weibull modulus is the parameter that represents the scatter of the distribution. Equation (4) can be linearized by calculating twice the natural logarithm, thus obtaining:

$$\ln\left(\ln\left(\frac{1}{1-F} \right) \right) = m \ln\sigma + \ln\frac{k\,S}{\sigma_0^m} \tag{5}$$

Fitting of the data shown in Figure 1, using linear regression, allows the calculation of the Weibull modulus corresponding to each strength distribution. The results are shown in Table 3: it is interesting to observe that the strengthening process is associated to a sensible decrease of the Weibull modulus, i.e. to an increase of the strength scatter.

		average	standard deviation	minimum	maximum
as-cut		257	47	140	346
A	4 h	331	71	158	465
	24 h	312	62	155	476
B	4 h	341	103	114	558
	24 h	304	63	151	437
C	4 h	441	155	131	505
	24 h	593	148	185	701

Table 2. Summary of the strength values (MPa) measured by biaxial flexure test on as-cut samples and on ion-exchanged glass (A, B, C).

The effect of ion-exchange appears clearer in Figure 1, although for samples treated in baths A and B the effect of time is not so evident. In any case, glasses exchanged in bath C show the best performances. One interesting aspect regards the different strengthening effect generated on glasses with different initial failure stress. As shown in Figure 1 (and reported quantitatively in Table 3) the tail of the distributions corresponding to low failure probability and limited strength are almost overlapped, regardless the ion-exchange process. This means that specimens characterized by large critical defects are substantially indifferent to the creation of a surface compressive stress whose extension is probably small compared to the depth of the critical flaw.

	A	B	C	as-cut
4 h	5.0	3.5	3.3	5.8
24 h	5.3	5.0	3.9	

**Table 3.** Weibull modulus of the strength distributions reported in Figure 1.

Some exemplary potassium concentration profiles measured by EDXS on the fracture surface of ion-exchange samples, chosen from very similar others, are shown in Figure 2. In this case, the potassium concentration recorded by line scan was scaled with respect to the intensity of the peak associated to the Kα line measured from surface analysis (Figure 3); as a matter of fact a ratio ≈0.25:0.4:1 was always recorded among the intensities of potassium Kα peak corresponding to specimens treated in bath A, B and C, respectively; in addition, some residual sodium was also detected on the surface of glasses treated in baths A and B.

Figure 2 shows that the depth involved in the ion-exchange process varies between ≈12 μm and ≈20-30 μm if the duration increases from 4 h to 24 h. On the basis of the failure stress measured in as-cut samples, the size of the critical flaw can be estimated using linear-elastic fracture mechanics from the expression:

$$c_F = \left(\frac{K_c}{\psi \, \sigma_F} \right)^2 \tag{6}$$

where K_c is the fracture toughness of the material and ψ the crack shape factor. Considering that biaxial tests were performed in laboratory air and that some sub-critical growth could have occurred before final failure, one can assume $K_c \approx 0.6$ MPa m$^{0.5}$ [18]; in addition, if semi-circular surface flaws are assumed, $\psi \approx 1.26$ [19]. Therefore, from the data in Table 2, values ranging from 3 μm to 12 μm can be calculated for the depth of the critical defect. It is consequently evident that the strengthening process, whose intensity decreases rapidly moving away from the surface, has very different effect on pre-existing flaws, the largest ones being almost unaffected by the ion-exchange. Moreover, the strengthening effect appears to be stronger on glasses treated in bath C that is responsible for a higher surface potassium concentration (and, therefore, for a more effective Na⁺-K⁺ interdiffusion) and for a deeper profile, especially at 24 h duration.

It is not easy to explain the discrepancies observed among glasses strengthened by using the three considered potassium nitrate baths. The differences among them are in fact relatively limited. Table 4 reports the major impurities in terms of metallic elements contained in the baths: salt A corresponds to substantially pure KNO₃; a larger amount of sodium is present
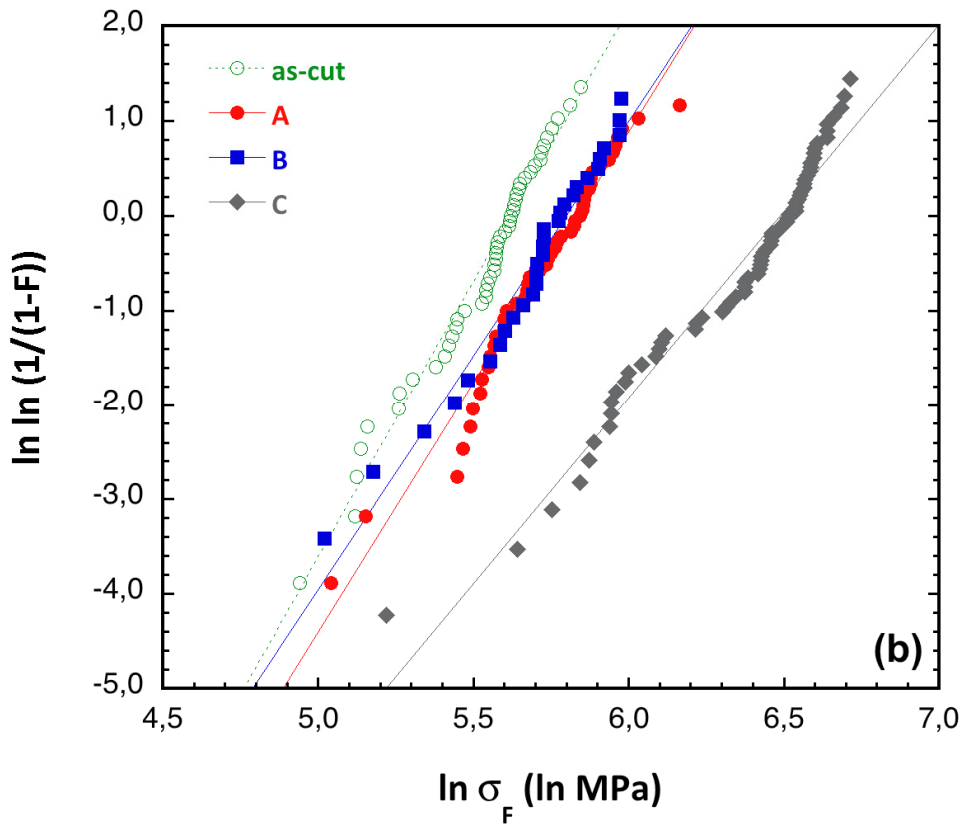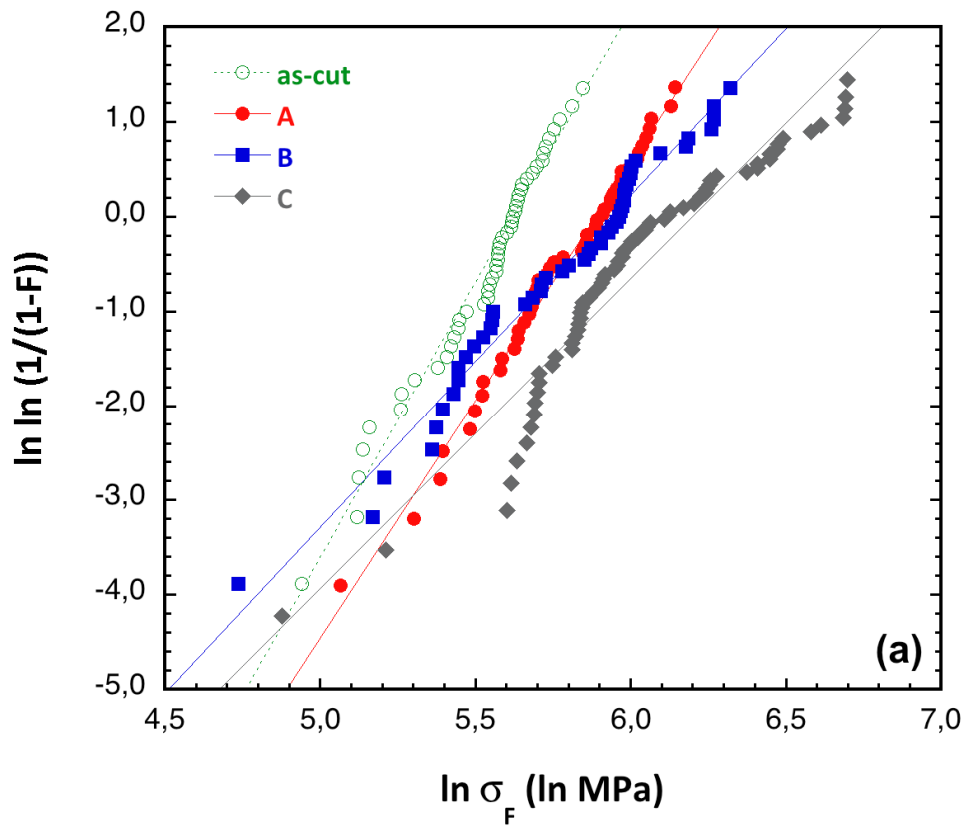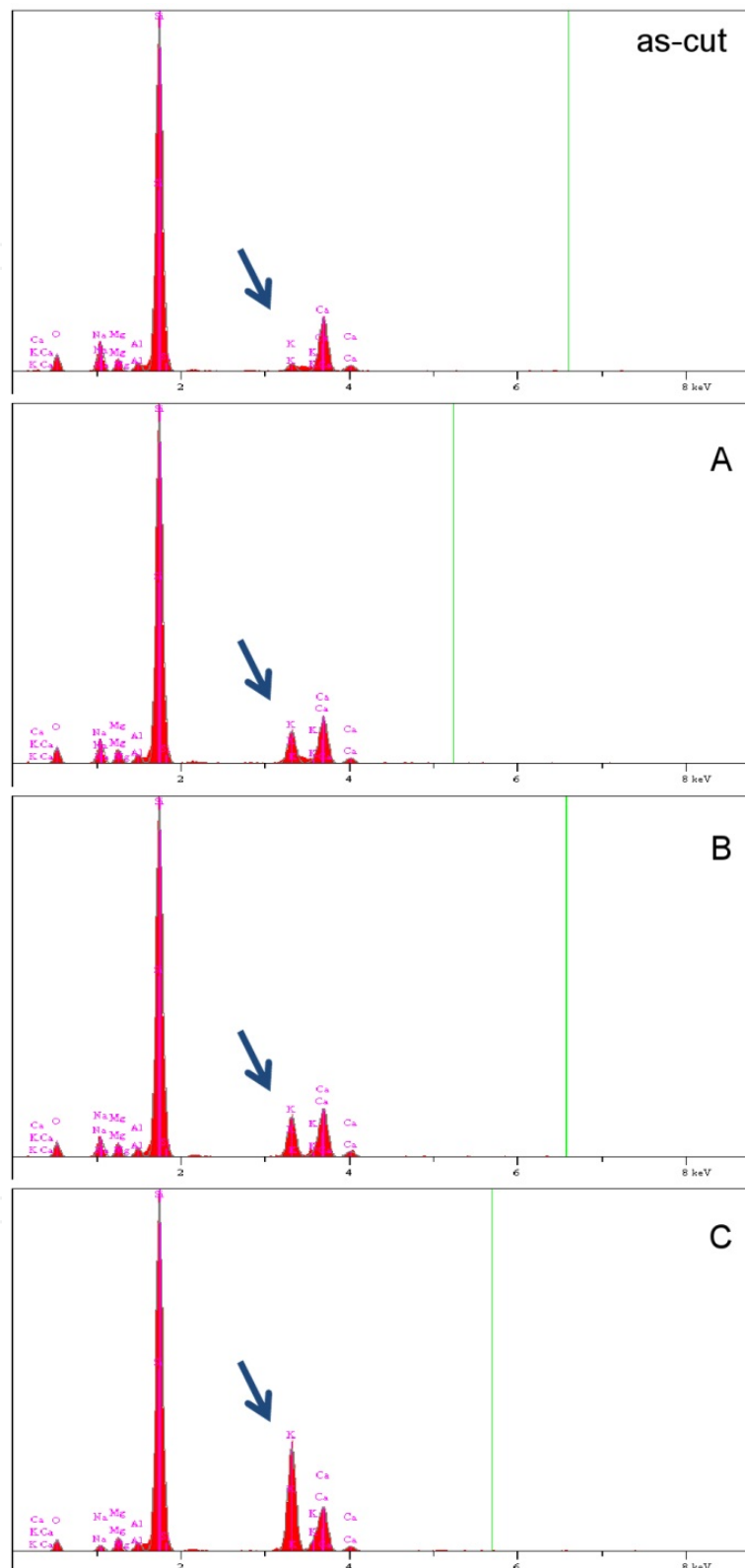
Figure 1. Weibull distributions of the strength for as-cut and ion-exchanged specimens: (a) 4 h, (b) 24 h. Straight lines represent fitting curves.
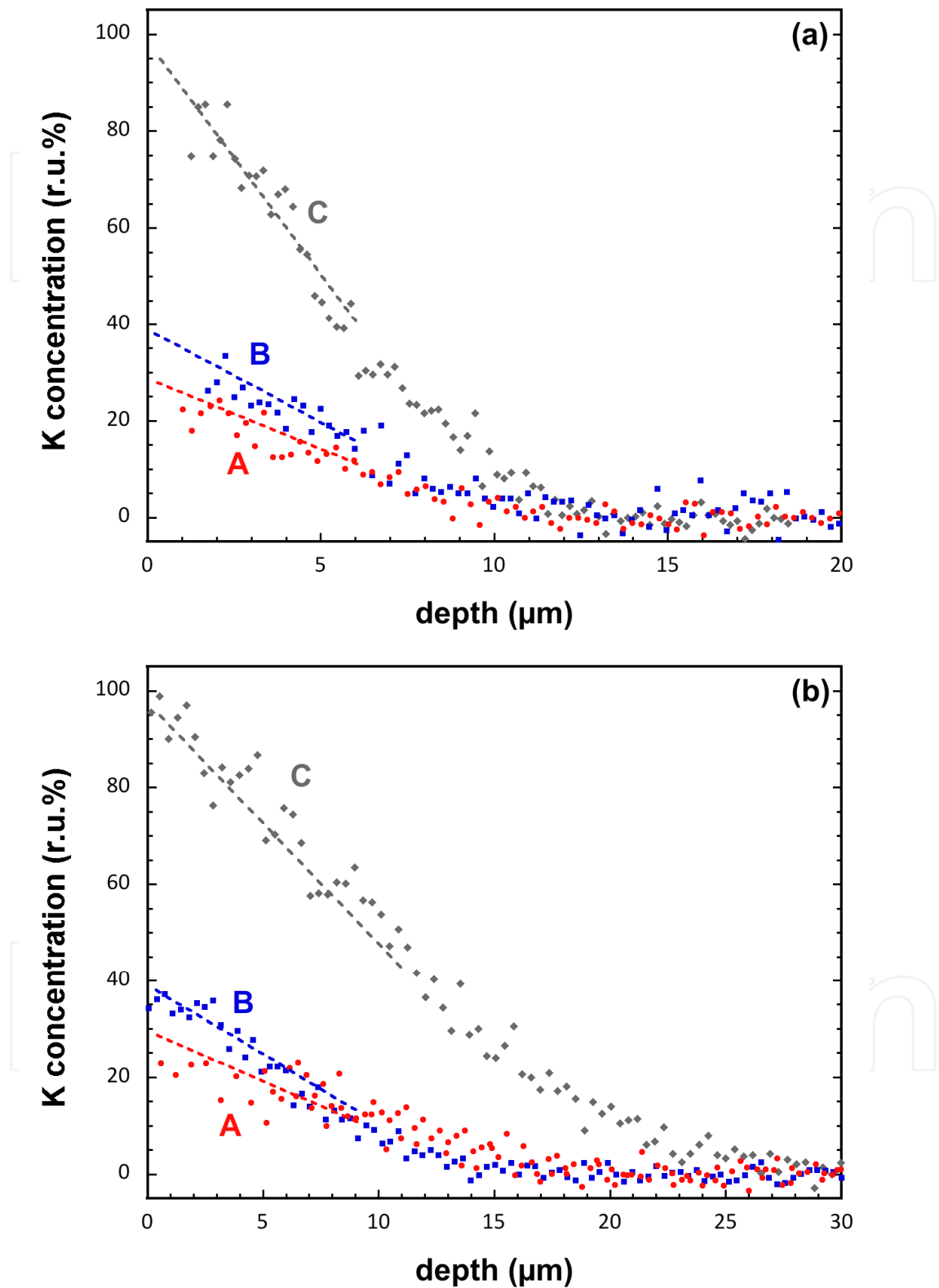
Figure 2. Potassium concentration profile as a function of the depth from the sample surface: (a) 4 h, (b) 24 h. Dashed lines represent tendency curves.

Figure 3. EDXS spectra recorded on the surface of samples subjected to ion exchanged for 24 h. The spectrum recorded on as-cut glass is shown for comparison. The potassium Kα peak is indicated by an arrow.

especially in bath C (around 0.5%) which corresponds to a NaNO₃ load of about 1.8%. Similarly, also the melting point of the three salts does not change substantially, varying from 335.5°C (bath A) to 334.6°C (bath B) to 331.0°C (bath C). On the basis of the results shown in Figure 2, it is possible to hypothesize that the slight difference among the three salts has substantial effect on the effective composition or activity of the K^+ ions on the glass surface, the interdiffusion coefficient being affected only to a limited extent. More precisely, the presence of Na^+ ion in the KNO₃ salt bath makes the exchanging process more effective.

The results obtained in the present work can be fitted in the more general framework regarding the effect of mixed salt baths on the chemical strengthening of silicate glass [12, 20-23]. Other previous works reported a sensible increase of the reinforcing effect when ion-exchange is performed in non-pure melted salts although a clear explanation of the physical/chemical mechanisms has not been given yet.

A certain number of different parameters has to be considered such as "impurities" in the glass composition, presence of non-metallic elements in the salt bath, interface interaction between glass and bath, effect of "tin side", exchanging pair of ions, structural and viscous relaxation. Additional analyses and tests are required for a deeper understanding of the problem; nevertheless, the results reported here point out interesting aspects regarding the salt bath composition for higher efficiency chemical tempering processes.

	A	B	C
Na	40±5	1100±50	5200±50
Ca	<1	<1	15±5
Cr			30±5
Zn	<1	<1	2±1

Table 4. Metallic elements content (ppm) in the KNO₃ baths.

4. Conclusions

The composition of the potassium nitrate salt bath in terms of impurities, mostly Na, seems to have an important role in the strengthening process of soda lime silicate glass by ion exchange. It has been found that chemical reinforcement is more effective when it is carried out in the bath containing the highest amount of sodium (≈ 0.5%). The results point out interesting practical and industrial aspects regarding chemical tempering processes with higher efficiency.

Author details

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