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Can annealing improve the chemical strengthening of thin borosilicate glass?

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ABSTRACT

In this work, we try to point out the influence of annealing prior to chemical strengthening on the mechanical strength of thin ion exchangeable alkali borosilicate glass. The effect of annealing at 425 °C on density, hardness and cracking behaviour were investigated. Then, as-received and annealed samples were subjected to ion exchange in a molten potassium nitrate bath at the same temperature for 4 h and the generation of compressive stress in glass was analyzed as well as the bending strength.

Annealing makes the glass denser, improves hardness and enhances the compressive stress build-up. However, bending strength of as-received and annealed glass after ion-exchange is substantially the same, this being probably attributed to the limited case depth if compared to surface flaws. Annealing before ion exchange does not appear to be a crucial factor in improving chemical strengthening efficiency in thin borosilicate glass.

1. Introduction

Ion exchange strengthening is nowadays a conventional approach to improve the mechanical properties of thin glasses such as those used in touchscreen devices and flexible electronics [1–3]. This technique, which is also known as chemical strengthening, is usually conducted by immersing an alkali (lithium or sodium) - containing glass in a molten potassium nitrate bath for several hours where the larger potassium ions diffuse into the glass and partially replace the alkalis. Stuffing larger potassium ions into the smaller alkali sites produces a compressive stress [1,2,4–8] and the generated surface compression is beneficial to neutralise the detrimental effect of surface defects on strength [4,8,9].

Glass composition and structure can influence sodium/potassium exchange and stress build up. The glass structure, in turn, depends on chemical composition as well as on thermal history [5,10]. Hyper-quenched (rapidly cooled) glass, such as thin glass or glass fibres, has lower fictive temperature and, consequently, different structure and physical properties compared to normally cooled one [11,12]. Interestingly, Svenson et al. reported that the densification of glass before ion exchange improves the compressive stress generation, while decreases the case depth [13], i.e. the depth at which the compressive stress is zero; these changes make the influence of such treatments on glass strength equivocal. In addition, it is known that structural transformations are reversible at elevated temperature and that thermal history effect is distorted if the glass is held for several hours at high temperatures below Tg, as it is required for chemical strengthening [8,14–16].

In this work, an attempt has been done to answer the question whether annealing can influence the chemical strengthening of thin sodium borosilicate glass.

2. Experimental procedure

Ion-exchangeable thin borosilicate glass sheets (D 263® T eco, with nominal thickness of 200 μm and provided by Schott AG) were used in the present work. Samples of different size were manually cut from the original sheets, washed with distilled water under ultrasonic agitation and with acetone and then air dried.

A portion of the specimens was annealed for 16 h in a muffle kept at 425 °C where they were placed in a stainless steel basket; then, they were removed immediately from the furnace and kept at room temperature to cool down freely.

The volume change upon annealing was determined by measuring the linear shrinkage. Specimens with dimensions of 10 × 60 mm^2 were used in this case; two thin scratches were produced at distance of about 40 mm and perpendicular to the longest sample axis. The scratches distance was measured by a profilometer (Hommel Tester T8000, Hommelwerke Gmbh, Schwenningen, Germany) before and after the annealing cycle. The density was also determined on the same samples by the Archimedes method; it was observed that the thickness variations were insignificant.

Differential scanning calorimetry (DSC) was used to measure the glass-transition temperature before and after the annealing. The

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analyses were performed by a differential scanning calorimeter, DSC2010, TA Instruments, USA, under N_2 (99.999%) flow. For each analysis, the zero line was initially measured by heating up and cooling down the empty aluminium pan and lid with heating rate of 10 °C/min. Then, glass powder with grain size lower than 200 μm (produced by manual crushing in an agate mortar) was used for the measurements. The samples were heated up to 600 °C with heating rate of 10 °C/min, kept 2 min to equilibrate at 600 °C and then cooled down at 10 °C/min; each cycle was repeated two times.

Samples with dimensions of 45 × 45 mm^2 were immersed in a molten KNO_3 bath, ACS grade Sigma-Aldrich >99.0, within a modified chemical tempering furnace, Lema TC 20S, Parma, Italy, at 425 °C for 4 h. The glass-to-salt ratio was always below 1:300. The samples were directly immersed into the salt bath without any preheating step; at the end of the cycle they were quickly removed from the bath and cooled down to room temperature.

The generated surface compression was measured according to ASTM C1279-13 norm using a surface stress meter, Luceo Co Ltd. (FSM 60 LE, Tokyo, Japan). Further evaluations were conducted by Vickers indentation using maximum load between 0.98 N to 19.62 N and 15 s holding time; the indentations were produced in lab air and optical micrographs were taken few seconds after indentation to avoid subcritical crack propagation. The optical micrographs were used to measure hardness and cracks length. Some indentations were also observed by Scanning Electron Microscope, SEM, Jeol JSM 5500, Japan.

The bending strength of samples was measured by ring-on-ring flexural tests using loading and support ring radius equal to 10 mm and 25 mm, respectively. The loading rate was kept constant at 5 N s^{-1}.

3. Results

The density of glass before and after annealing for 16 h at 425 °C is reported in Table 1 and we see that it increases after annealing. The mass change during the treatment is, in practice, zero and it can be ignored; therefore, the volume shrinkage upon annealing can be estimated as:

$$\frac{\Delta V}{V_0} = \frac{\rho_{Ann} - \rho_{As-rec}}{\rho_{Ann}} \quad (1)$$

where ΔV and V_0 are the volume change and the initial volume of glass, respectively, ρ_{Ann} and $\rho_{As\text{-}rec}$ being the density of annealed and as-received glass, respectively. By using the data in Table 1, the volume shrinkage is estimated about 1.18%, which is, as expected, about three times as large as the measured linear shrinkage equal to 0.38% ± 0.08% as it was determined by the profilometer measurements.

Fig. 1 shows the DSC plot in terms of heat flux and its derivative for as-received and annealed glass measured during the first and the second scan; during the first scan, the onset temperature for the annealed sample is clearly lower than in the as-received glass. The derivative gives a clear picture of the glass-transition, which appears as a peak whose maximum is associated with the glass transition temperature (Tg); one can clearly observe that Tg decreases from 574 °C to 562 °C after annealing. The shape of transition peak in the derivative plots can furnish some additional information on the glass structure: smaller peak is related to a structure similar to the liquid or, in other words, a higher fictive temperature [5]. Therefore, the structure of as-received glass, which is characterised by a smaller transition peak, is more similar to the melt with identical composition [17].

Table 1
Density of the as-received and annealed glass; the numbers between parenthesis present the standard deviation measurements.

	Density (g cm^{-3})
As-received	2.50 (0.01)
Annealed	2.53 (0.02)

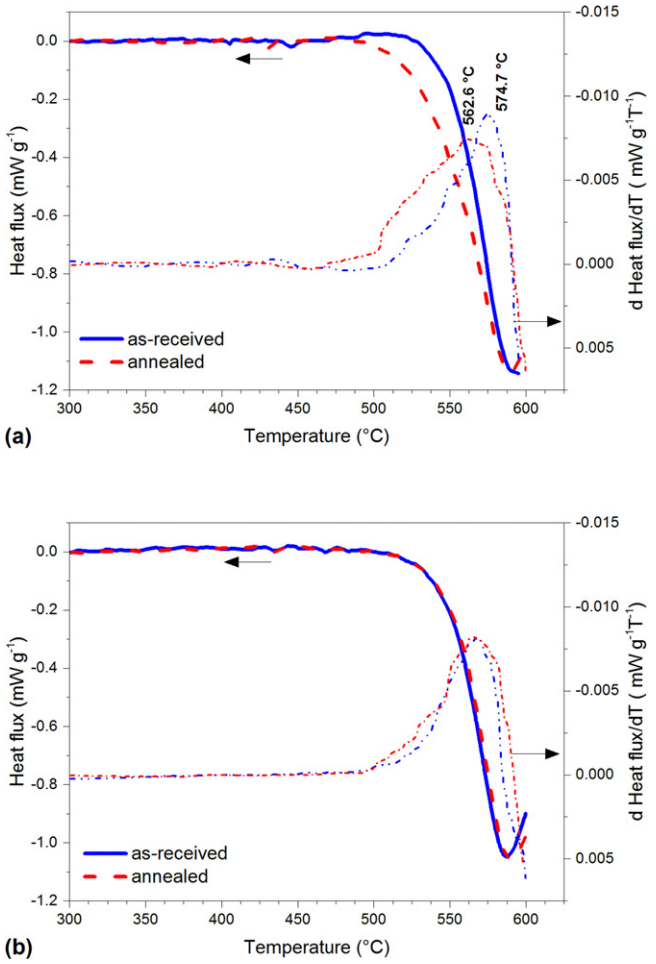

Fig. 1. Normalized heat flux and its derivative (from DSC analysis) against temperature for as-received and annealed glass; (a) first upscan, (b) second upscan.

It is interesting to observe that the DSC plot is identical for as-received and annealed glass during the second scan. As a matter of fact, the glass structure depends on the cooling rate from the liquid structure in temperature higher than Tg, and, hence, it is the same for both glasses when the cooling rate is equal to 10 °C min^{-1} [12,18].

Fig. 2 shows Vickers hardness of as-received and annealed glass measured with 1.96 N load before and after ion exchange at 425 °C for 4 h. Annealing and ion exchange are responsible for higher glass hardness. It is remarkable that ion exchange of annealed samples intensifies the hardness increase and produces quite harder material. Some exemplary indentations produced on as-received glass are shown in Fig. 3. Radial cracks are visible around the hardness imprint when load in excess of 1.96 N is used; moreover, we observe that indentations produced using load larger than 4.91 N exhibit light birefringence patterns around the indentation, this indicating the formation of lateral cracks beneath the surface.

Fracture toughness can be estimated from the crack length (c) at specific indentation load (P) using the well-known equation [19]:

$$K_C = \frac{\chi P}{\sqrt{c^3}} \quad (2)$$

where χ is a material constant depending on hardness and elastic modulus and typically assumed equal to 0.06 [20].