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Influence of residual compressive stress on nanoindentation response of ion-exchanged aluminosilicate float glass on air and tin sides

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ABSTRACT

The effect of the surface compressive stress (CS) on the hardness and Young's modulus of the ion-exchanged aluminosilicate float glass on air and tin sides are investigated. The hardness and Young's modulus are experimentally measured by nanoindentation. As a result, the surface hardness and Young's modulus of aluminosilicate float glass can be enhanced by chemical strengthening. The hardness increases with an increase in the CS, whereas Young's modulus is not obviously influenced by CS. The hardness and Young's modulus on the air and tin sides are almost the same before ion exchange. However, the tin side always has greater hardness than the air side after the ion exchange. The results would be useful in guiding the strengthening process of float glass by one step ion-exchange or two step ion-exchange to obtain engineered stress profile (ESP) glasses.

1. Introduction

The exchange of large alkali ions from a molten salt bath with comparatively smaller host alkali ions in an alkali-containing glass at temperature below the glass transition produces a compressive stress on the glass surface, which results in glass strengthening [1,2]. Despite the fact that it was invented approximately fifty years ago [3], chemically strengthened glass has failed to capture large markets until recently when large specialty glass companies launched chemically strengthened float glass such as Corning® Gorilla® Glass [4], Asahi Dragontrail™ [5], and Schott Xensation™ [6,7]. Such aluminosilicate glass has been the main material for fabricating touch panels of popular display devices. Scratch-proof properties, an important guideline for touch panels, are closely related to the material hardness. The hardness can be enhanced using an ion-exchange technique because of the change in the bond energy and density on the ion-exchanged glass surface with a high compressive stress [8,9]. Thus, an investigation of the influence of compressive stress on the hardness of the ion-exchanged glasses is important.

Further, the primary source of all flat glass for automotive and architectural applications is the glasses produced by the float process, which is first demonstrated by Pilkington [10]. This process involves the delivery of molten glass from a melting furnace onto an enclosed bath of molten tin, gradually decreasing the temperature in the float chambers and annealing lehr, and finally cutting and packing [11,12]. Due to this process, the molten tin diffuses into the bottom surface of the glass that produces two chemically different sides, often referred to as the air and tin sides. The composition and the related structural difference between the two sides may result in different compressive stresses and the depths of the stress layer, which can impact the glass properties [13,14]. Consequently, the elucidation of the influence of compressive stress on the nanomechanical properties on the air and tin sides is very meaningful in controlling the float glass properties. However, the difference between the hardness of the ion-exchanged float glass on the air and tin sides remains unclear thus far.

In this study, the nanoindentation technique is employed to investigate the hardness and Young's modulus of the float aluminosilicate glass on both air and tin sides. The surface hardness and Young's modulus of aluminosilicate float glass can be enhanced by chemical strengthening. The hardness increases with an increase in the compressive stress, whereas Young's modulus is not obviously influenced by compressive stress. The hardness and Young's modulus on the air and tin sides are almost the same before ion exchange. However, the tin side always has greater hardness than the air side after the ion exchange. The results provide useful information for understanding the mechanical properties of the aluminosilicate float glass.

2. Experimental procedure

The glass used in this work is a 2.2-mm-thick float glass with a chemical composition of 67.0 wt.% SiO_2, 5.0 wt.% Al_2O_3, 14.9 wt.% Na_2O, 9.2 wt.% MgO, and 3.9 wt% K_2O with the tin and air sides identified. The ion-exchange process is carried out in an electric furnace at different temperatures (410, 430, 450, 470, and 490 °C) for different times (1, 4, 8, 12, and 16 h) to produce different compressive stress. Before the ion exchange, all glass specimens are annealed at 550 °C for 8 h to remove residual stress in the glasses. In the ion-exchange process, glass specimens are immersed into molten pure KNO_3 (purity > 99.9%), and the alkali ions from the glass surface are exchanged with those from

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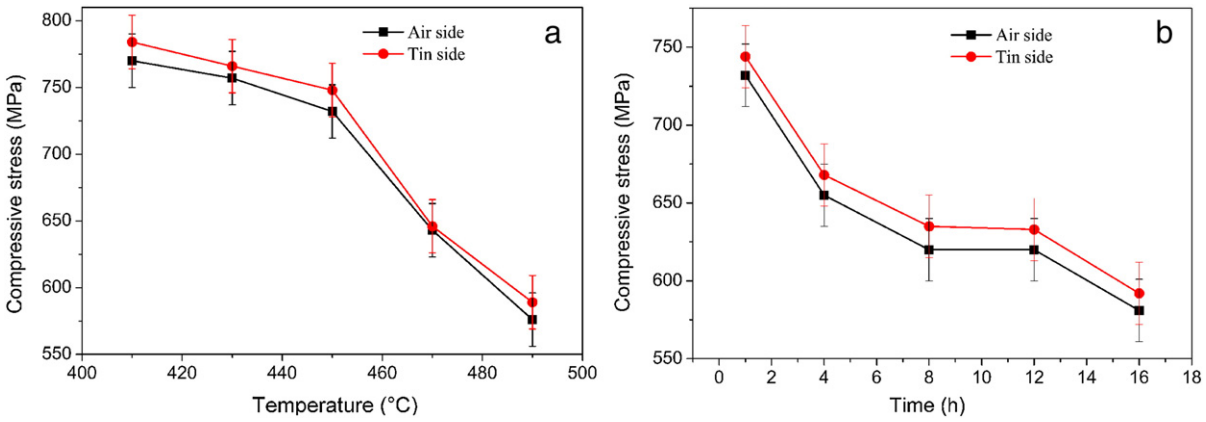

Fig. 1. Compressive stress on the air and tin sides of ion-exchanged specimens: (a) at different exchange temperatures for 1 h, and (b) at 450 °C for different exchange times.

the molten salt. The glass surfaces are carefully cleaned with deionized water at the end of each ion-exchanged cycle.

The compressive stresses (CS) of the specimens after chemical strengthening are measured by FSM-6000LE. The ion concentrations of the air and tin sides of the raw and ion-exchanged specimens with different compressive stresses are measured by X-ray photoelectron spectroscopy (XPS). In order to avoid any build-up of a contamination layer on the glass surface, the samples were fractured in situ just before measurement in an ultrahigh vacuum preparation chamber. XPS data were obtained using a PHI Quantera SXM system. An Al Kα radiation was used. Binding energies are referenced to the carbon 1 s peak set at a binding energy of 284.6 eV. The insulating surface required the use of a low energy electron flood to compensate the surface charging. Atomic concentrations based on peak area were calculated using the software XPS-Peak. This software corrected the peak area for the sensitivity factors for each photoelectron line. A Shirley background subtraction and a Voigt lineshape, which is a mixed Lorentzian–Gaussian peaks (L–G ratio = 80%), were used to fit the peaks in each spectrum. To find a best fit of the data for each composition, the position, width and intensity were varied several times during the binding energy peak fitting. The confidence interval which is used for the binding energy peak fitting is 95%. Three samples at each CS level were analyzed in order to confirm the reproducibility of the results and therefore the standard derivation can be obtained (±5%).

The nanoindentation data in this article were analyzed using the procedure developed by Oliver and Pharr (referring to it as OP method) [15] which is widely used in current researches and tests. The OP method of nanoindentation analysis uses the unloading portion of the force–displacement curve and relies on an accurate knowledge of the indenter geometry. The elastic modulus and hardness are derived from the following equations:

$$H = \frac{P_{\max}}{A} \tag{1}$$

$$\frac{1}{E_r} = \frac{\left(1-\upsilon^2\right)}{E} + \frac{\left(1-\upsilon_i^2\right)}{E_i} \tag{2}$$

In the above equations, P is the applied load, A is the contact area of the indenter, E and υ are Young's modulus and Poisson's ratio for the specimen, E_i and υ_i are the same parameters for the indenter and E_r is defined as a reduced modulus which can be get from the equation:

$$S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A_c} \tag{3}$$

The contact stiffness S can be measured from the unloading data and the projected contact area A can be computed from the relation:

$$A(h_c) = 24.5h_c^2 + \sum_{i=1}^{8} C_i h_c^{\frac{1}{2^{i-1}}} \tag{4}$$

In the equation, C_1 through C_8 are constants derived from the calibration process and they describe deviations from the Berkovich geometry due to blunting at the tip. h_c is the contact depth, which relates to

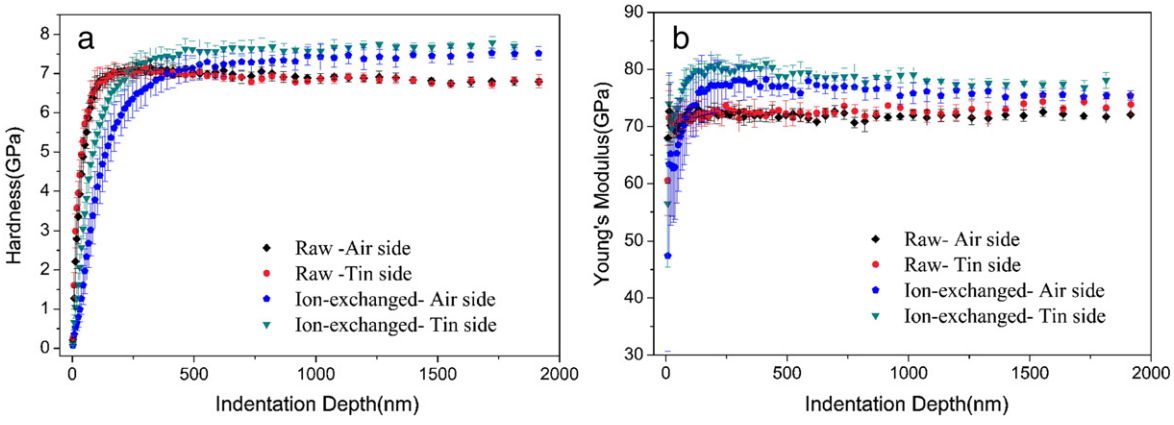

Fig. 2. Mechanical properties, as a function of the indentation depth of the raw and ion-exchanged glass: (a) hardness; (b) Young's modulus.