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Selective Stress Relaxation on Chemically Strengthened Glass Sheets for Conventional Wheel Cutting

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We introduce, for the first time to the best of our knowledge, the use of variable frequency microwave (VFM)-assisted second ion exchange to selectively modify the compressive stress CS in chemically strengthened glass sheets, which allows for separation of these glass sheets into smaller pieces using a conventional cutting tool. The CS in paste-coated zones, in the regions where it is desired for separation of the glass sheets, was successfully manipulated via VFM-assisted second ion exchange, substituting the larger alkali ions in glass by smaller ions of the paste. Its effect on chemically strengthened glass was characterized using a strain viewer, an optical microscope, and an electron probe microanalyzer. We also report on the scribability and breakability across the stress relaxation zones. The results reveal a CS loss of only 3%, from 677 to 656 MPa, in the paste-uncoated zones, and complete CS relaxation, down to 0 MPa, in the paste-coated regions. The areas of relaxed CS enable the separation of the strengthened glass sheets using conventional wheel cutting.

I. Introduction

Chemical strengthening of glass sheets by ion-exchange processes involves the generation of compressive surface stress by substitution of smaller alkali ions in glass by larger ions. When a smaller ion is substituted by a larger ion, the latter is literally squeezed into the surface, thus rendering residual compressive stresses at the surface, with a balancing tensile stress in the interior.[1–5] The recent exponential increase in the use of display-related products such as smart phones, tablets, and TVs has necessitated the use of high ion-exchange glasses. These glasses have a high level of compressive stress (CS) and a high depth of the compressive layer (DOL), and are hence used to protect devices against damage from mechanical impact and to increase glass reliability against common handling flaws.

One of the main issues in chemical strengthening is an expensive production process. The high costs are a result of extended bath immersion to achieve a sufficient compressive depth. To reduce cost without compromising on effectiveness, new innovative manufacturing processes involving the use of additional energy, such as ultrasonic-, microwave-, and electric field–assisted ion-exchange processes, are considered to enhance the diffusion rate.[6–8] Another emerging issue is the development of a suitable cutting process after chemical strengthening to streamline manufacturing processes and to improve production efficiencies.[9] There are a few reports on separating strengthened glass into smaller pieces after ion exchange via eliminating compressive layer.[10,11] The compressive layer near the surface of the glass is relatively narrow, on the order of ~50 μm, and originates from the balancing tension at the center of the glass. This balancing tension provides the necessary energy for the propagation, and bifurcation of cracks during breakage.[12,13] An interesting fact is that the tension at the center is determined by the glass thickness and the magnitude and shape of the CS profile. Thus, if the outer compressive layer is removed by chemical etching with HF acid, mechanical polishing, or sand blasting, mechanical cutting of ion-exchanged glass is possible, irrespective of the DOL and the level of CS.[14,15] However, the processes of chemical or mechanical removal of the compressive layer make glass handling difficult, as they could lead to contamination from chemicals and glass particles. For this reason, the development of a process for the elimination of CS without physical deformation of the glass presents a challenging topic and is worth studying.

In the present research, we introduce a variable frequency microwave (VFM)-assisted second ion-exchange method to selectively modify the CS of chemically strengthened glass sheets and, subsequently, thus separate strengthened glass sheets into smaller pieces with a conventional cutting tool. The effects of the microwave energy on chemically strengthened glass were evaluated by analyzing the residual CS and the depth profile of alkali ions.

II. Experimental Procedure

The glass used in this study is a commercial alkali aluminosilicate (Corning 2317 Gorilla® Glass, Corning, NY) especially designed for ion exchange up to a great depth. The strengthened glass with a CS of 650–700 MPa and a DOL of 40–43 μm was obtained from DAESEUNG Corp (Seoul, Korea).

The paste used for VFM-assisted second ion exchange, for substituting the larger alkali ions in strengthened glass with smaller ions to reduce the CS, was prepared by dissolving 91.2 g of sodium nitrate [$NaNO_3$; Sigma-Aldrich Co (Louis, MO). CAS No: 7631-99-4] in 100 mL of deionized (DI) water. Then, a slurry was produced by adding 20 g of zinc oxide [ZnO; Samchun Pure Chemical Co., LTD, (Pyeongtaek, Korea) CAS No: 1314-13-2] to 44 mL of the above solution. The prepared paste was subsequently coated uniformly on both sides of a glass substrate in a striped pattern (20 mm width and 100 μm thick), as shown in Fig. 1(a), and dried at room temperature for 1 d.

A VFM/infrared (IR) hybrid system (manufactured by Lambda Morrisville, NC), with a power of 1.6 kW and a broadband microwave frequency range 5.85–6.65 GHz, was

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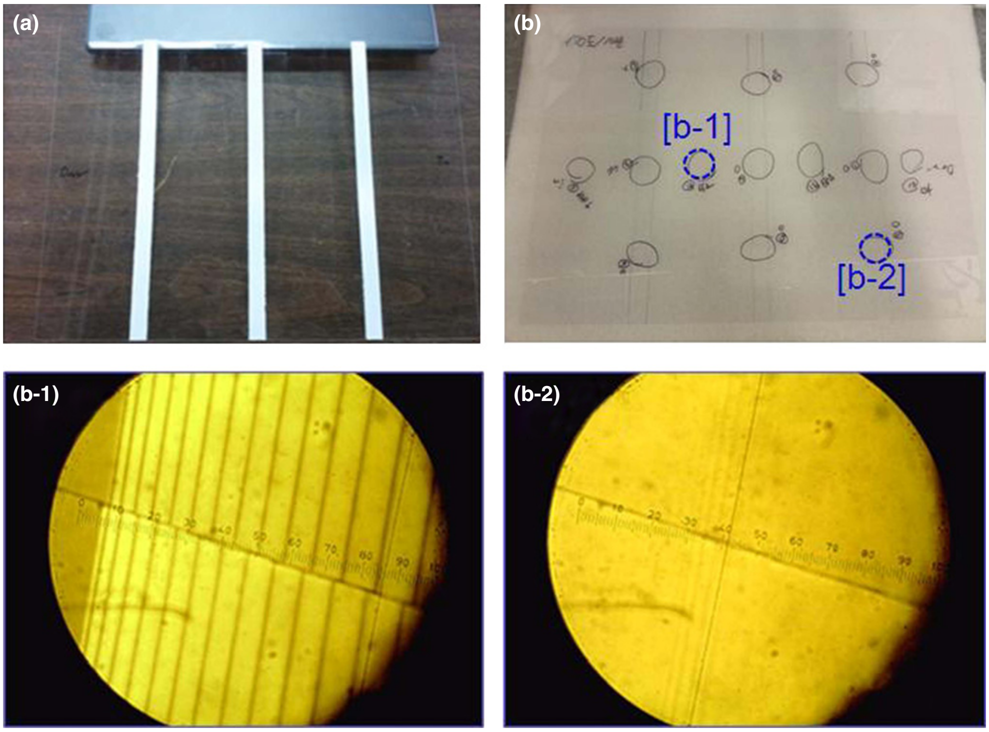

Fig. 1. The effect of variable frequency microwave (VFM) irradiation on the compressive stress in chemically strengthened glass. (a) VFM-irradiated glass (300 mm × 400 mm × 0.7 mm), (b) cleaned glass, [b-1] optical fringe patterns obtained for paste-uncoated zones, and [b-2] optical fringe patterns obtained for paste-coated zones.

used to heat only the paste-coated zone up to a target temperature, whereas uncoated areas remained at a low temperature. In the experiment, the sample was preheated up to 200°C–250°C by applying conventional heating to prevent catastrophic breakage from thermal shock and to improve the interaction between the paste and microwave energy. Subsequently, microwave energy was supplied along with IR radiation to ensure that further heating is restricted to the paste-coated zone up to the target temperature of around 400°C–500°C for 10–15 min. After cooling down to room temperature, the sample was washed with water to remove the paste.

The CS and the DOL were analyzed using a strain viewer (FSM-60LE; Orihara, Toshima, Japan) on both sides of the glass. The amount of stress relaxation within the paste-coated zone and stress loss of the paste-uncoated area was measured. The cutting test was carried out by MDI-Korea (Mitsuboshi Diamond Industrial Co. LTD, Incheon, Korea) specializing in supplying cutting equipment. The scribed glass surface and the broken fracture surface were observed using an optical microscope (MM6C-PC310-2; Olympus, Tokyo, Japan). The concentration of the alkali ions Na^+ and K^+ before and after second ion exchange was analyzed by line scanning with an electron probe microanalyzer (EPMA; JXA8900R JEOL, Tokyo, Japan).

III. Results & Discussion

Figure 1 shows the images of a sample before and after VFM-assisted selective second ion exchange. After the treatment, the paste coated on top of the glass surface was easily washed out and no damages, such as physical distortion and optical strain, were observed. To discern the stress relaxation zones, black lines were marked on each glass sheet, as shown in Fig. 1(b). The CS was automatically calculated from the offset in position between the upper fringes [corresponding to the transverse magnetic (TM) polarization] and the lower fringes [corresponding to the transverse electric (TE) polarization], and the DOL was calculated from the number of fringes and the width of the fringe patterns, based on TM mode data.[16,17] The CS was measured at 14 spots on each side of the glass substrate, and of them, four spots were used for the measurements without paste coating. VFM irradiation made the optical fringe patterns disappear at the paste-coated zones and only one to two spots of nine measurements showed very weak optical fringe patterns, which did not even allow for the determination of the residual stress, as presented in Fig. 1 [b-2]. On the other hand, no obvious changes in the optical fringe patterns of the paste-uncoated zones could be observed in Fig. 1[b-1]. This result proves for the first time that selective stress relaxation on chemically strengthened glass via VFM-assisted second ion exchange is possible without physical distortion and optical strain.

The values of the CS and the DOL are summarized in Table I. The CS of the paste-uncoated zones decreased slightly by 3%, from 677 to 656 MPa. Likewise, the DOL slightly increased by ~2%, from 43.7 to 44.6 μm. In the case of the paste-coated zone, most of the regions witnessed a complete relaxation of CS, down to 0 MPa, and only a few regions showed a residual stress below 100 MPa.

Concerning the stress reduction behavior (of ~3%) observed at the paste-uncoated zones, we suspect that there should be an interaction between the microwave energy and the glass structure. Glass is well-known to be a material transparent to microwave frequencies.[18] However, if the glass temperature increases, the interaction between the microwave radiation and the glass structure gets activated, owing to an increase in the dielectric loss in glass as a function of temperature.[18] Based on the glassy structure, it should be noted that

Table I. Comparison of Compressive Stress Before and After Variable Frequency Microwave Irradiation

		Before	After	Ref.
Uncoated surface	CS (MPa)	676.8 ± 19.04	656.3 ± 22.7	3% (Loss)
	DOL (μm)	43.7 ± 2.0	44.6 ± 2.0	2% (Deep)
Coated surface	CS (MPa)	676.8 ± 19.04	0 ~ 100	100 ~ 5% (Relaxation)

the ionic mobility of elemental glass components, especially alkali cations like Na^+ and K^+, represents an activated process implying that the squeezed ions in the compressive layer may be brought into movement, thereby resulting in stress relief. The temperature achieved by conventional heating to prevent thermal shock from an abrupt temperature change may be considered as an additional reason for the minor stress relief. However, a temperature below 250°C presumably affects the increasing dielectric loss of glass, thereby inducing increased microwave energy absorption, rather than decreasing

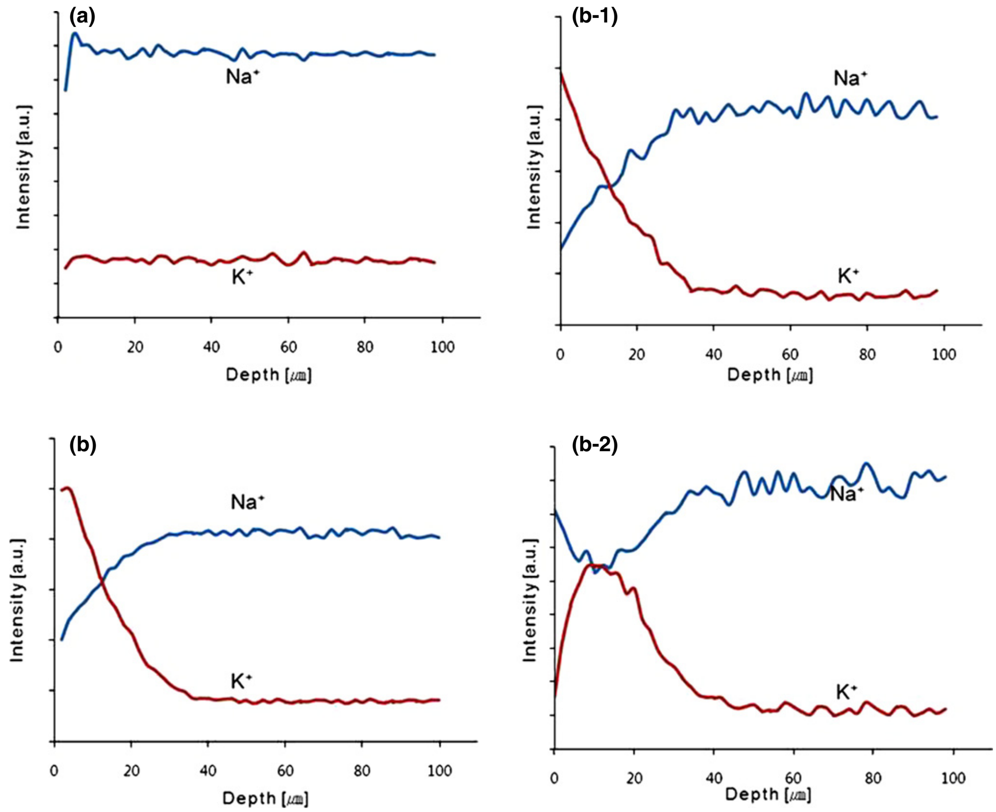

Fig. 2. Potassium and sodium concentration profiles as a function of the depth. (a) a mother glass, (b) a chemically strengthened glass, [b-1] a paste-uncoated area, and [b-2] a paste-coated area after variable frequency microwave irradiation.

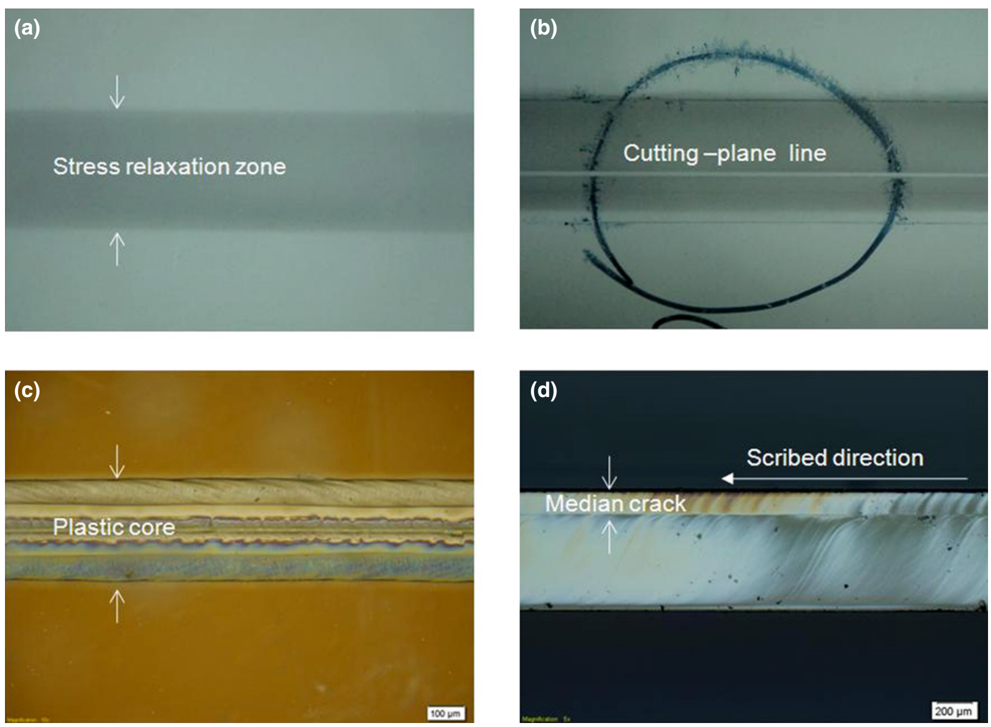

Fig. 3. Scribability and breakability of chemically strengthened glass after selective compressive stress relaxation. (a and b) top view of the glass taken with polarized light, (a) before and (b) after cutting, (c) top view of the glass scribed by a normal cutting wheel, and (d) cross-sectional view of the glass separated after breaking.

the CS because this temperature is probably too low to cause a thermally activated structural relaxation.[18,19]

The potassium and sodium concentration profiles were analyzed to understand the stress relaxation mechanism and were plotted as a function of the depth, as shown in Fig. 2. The plots present clearly that the ion profiles within paste-uncoated zones did not change whereas the profiles of paste-coated areas varied significantly after selective second ion exchange. The profile looked similar to the engineered stress profile glass reported by Shen and Green[3] From Fig. 2[b-2,] we suggest that there is a substitution reaction between the strengthened glass and the Na^+-containing paste right below the glass surface as follows: K^+ (glass) + Na^+ (paste) → Na^+ (glass) + K^+ (paste). The second ion exchange occurs only at the paste-coated surface and its depth is around 15 μm. Here, it should be noted that all CS has been relaxed even though the depth of substituted Na^+ ions only reached ~15 μm. We believe that there are complex mechanisms involved in the release of compressive stresses. The mechanisms for a selective stress relaxation could be discussed in terms of the characteristics of microwave heating. The paste containing Na^+ ions is a good absorber of microwave energy implying that microwave radiation can interact directly with Na^+ ions in the paste and cause heat by friction originating from vibrations of Na^+ ions. Therefore, the temperature within a paste-coated zone is much higher than that of an uncoated region, thus resulting in a locally elevated temperature that promotes the chemical reaction between Na^+ ions in the paste and K^+ ions in the glass. This process results in a thermal release of CS and a rearrangement of the squeezed glass structure via direct coupling to the microwave radiation.

Figure 3 shows a typical top view of the glass surface obtained from a strain viewer after the selective second ion-exchange process and a side view of cleanly cut glass after scribing and breaking. The out-cut cutting test was performed employing a conventional cutting wheel and the scribe load was around 0.2–0.25 MPa. The median crack depth is constant within the plastic core zone and the Waller lines exhibit a uniform curvature without irregular cracks.[20] These results prove that a chemically strengthened glass with a deep DOL and a high level of CS can be cut into a designed shape by relaxing the CS by the selective second ion exchange.

IV. Conclusions

The local CS of chemically strengthened glass sheets was successfully modified. The paste materials coated on top of the glass surface play a key role in relaxing the CS by absorbing microwave energy, resulting in a locally elevated temperature that promotes the chemical reaction between Na^+ ions in the paste and K^+ ions in the glass. This reaction leads to a thermal release of the CS and a rearrangement of the squeezed glass structure via direct coupling of the glass structure with the microwave radiation. The selective stress relaxation allows for a separation of the chemically strengthened glass by conventional wheel cutting. We expect this result to have significant potential in the development of shape-conformable strengthened glasses.

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