

Chemical treatment to improve usable strength of Ion-exchanged cover glass

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Glass leaching, including dissolution and hydrolysis, was introduced to mend surface flaws in ion-exchanged glass. The leaching behavior on the glass surface was analyzed by using a spectrophotometer, AFM, a confocal LCM, a surface stress meter and TEM. The results revealed that a silica-rich nano layer was formed on the surface of the glass after soaking in an acidic solution by dissolution of alkali ions from glass surface, and the formed layer including the flaws on the surface of the glass were completely removed after being exposed to an alkaline solution. We also found that leaching an aqueous solution increased the mechanical strength dramatically in ion-exchanged glass without degradation of surface quality.

Keywords: Ion exchange, Cover glass, Usable strength, Chemical treatment, Silica-rich layer.

Introduction

Glass is now commonly used in many portable electronic displays, mobile phones and tablets, as a protective cover for the devices. The ion exchange process, Nullification of Surface Damage, is generally conducted to improve the mechanical properties which are dependent on the compressive stress at the surface and the depth of penetration of larger ions. Thus far, the ion exchange method has been widely used for the strengthening of cover glass because the generated compressive stress prevents crack propagation in glass adequately. However, due to recent requirements for thin, light-weight and unbreakable devices, the glass used is getting thinner and thinner, and the ion exchange method has limitations to meeting the unbreakable glass requirements due to unavoidable nano damages on the surface of the glass which are more critical when the local bending is made by blunt impact [1-6].

In order to meet the requirements, functional coatings are used on glass with organic and inorganic materials to minimize the stress concentration in the crack tip. Teisseire et al. reported that edge-strengthening of flat glass increased with acryl coating [7]. Also, there are several reports with silica-like coating, diamond-like coating and sapphire-like coating to increase the glass hardness as well as the glass strength by reducing the role of stress corrosion at the crack tip that is promoted by moisture at the surface [8-10]. However, the organic coating is accompanied by hardness reduction as well as reliability issues, and the inorganic coatings have some side effects such as transmittance reduction, reduction

of compressive stress due to the relatively high processing temperature, cost increase, etc. The most critical problem of the coating method is that it couldn't be free from surface damages due to the inability to mend surface damage thoroughly [11].

Chemical etching or healing, to remove surface damages and bring back a pristine state, is studied; but it has not met the surface quality required. Etching with hydrofluoric acid is a well-known and easy method to increase glass strength by enlarging the radius of the crack tip [12-14]. However, the etched surface becomes very uneven and the crack maintains its original depth as etching proceeds. The greatest disadvantage is that the microcracks become visible etch pits. Thus it is not very attractive as a commercial technology [15-17].

Therefore in this study, we introduced the chemical cleaning method of using glass leaching to include glass dissolution and hydrolysis. A silica-rich nanolayer is placed on the surface of the glass reaching the lowest depths of the flaws, and it is formed uniformly by exposing the glass to an aqueous acid solution and leaching the alkali ions. The formed silica-rich nanolayer is then removed completely by soaking the glass to an aqueous alkaline solution. The formation of silica-rich nanolayer is confirmed and characterized by using UV-VIS spectra, AFM, LCM and TEM. The thickness of nanolayer is varied with time, temperature, and pH. The tested glass has shown excellent mechanical performance without a trade-off among the strength, surface quality, and hardness.

Experimental Procedure

The samples of glass used in this study are commercially available alkali-aluminosilicate (Corning Gorilla 3 & Gorilla 5 Glass, Corning, USA) specially designed for ion exchange up to a great CS (Compressive Stress)

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and deep DOL (Depth of Layer). The samples of glass were cut to desired size (typically mobile phone with dimensions 70 mm × 150 mm) and put through a mechanical machining and surface finishing process to make a 2D or 2.5D shape.

The samples of glass were strengthened by ion exchange processes with the recipe provided by the glass maker. The Gorilla 3 samples were treated with a single step process and the Gorilla 5 samples were strengthened by a 2-step process. Prepared samples satisfied all specifications required for a cover glass.

Acidic solutions were prepared with the three different acids (H_2SO_4 70% Hangseong Chem, CAS NO: 7664-93-9, HCl 35% Hangseong Chem, CAS NO: 7647-01-0, HNO_3 60% SN Chem CAS NO: 7697-37-2) and distilled water. Specimens were immersed in the acidic solution (60 liter) in a plastic bath. The solution was stirred with a Teflon-coated stirrer and heated with a Teflon-coated heater during the experiment, and the leaching behaviors were monitored as a function of the time and temperature. The formed silica-rich nanolayer was removed with alkaline solution prepared by using NaOH (Soda Flakes 98% YoungJin Chem.) and distilled water.

The formation and removal of the silica-rich nanolayer was confirmed and characterized by using spectrophotometer (CM-3600d, Konica Minolta), AFM (NX-20,

Park Systems), LCM (Laser Con-focal Microscope), FSM (a surface stress meter FSM-6000LE; Orihara, Toshima, Japan) and TEM. The thickness of the silica-rich nanolayer was dependent on time, temperature, and pH level of the solutions. Its effect on the mechanical property of glass was tested with a dynamic impact test with a 150 g steel ball.

Results and Discussion

When ordinary glass was exposed to an aqueous solution, alkali ions from the glass were extracted into the solution, and an alkali deficient leached layer that is also a silica-rich nanolayer is formed on the glass surface. The thickness of silica-rich nanolayer depends on the glass composition and test conditions such as time, temperature and pH of the solution [18-21]. One interesting finding is that the silica-rich nanolayer formed on glass surface became susceptible to decomposition in alkaline solution. Figure 1(a) shows the processes when a sample of glass is exposed to an acidic solution as well as alkaline solution. Here a silica-rich nanolayer was formed on glass surface including the flawed areas with a thickness of 200~1000 nm in order to improve the glass strength further. This thermodynamic prediction has been verified by Shamy, Lewins and Douglas [22]. To observe the

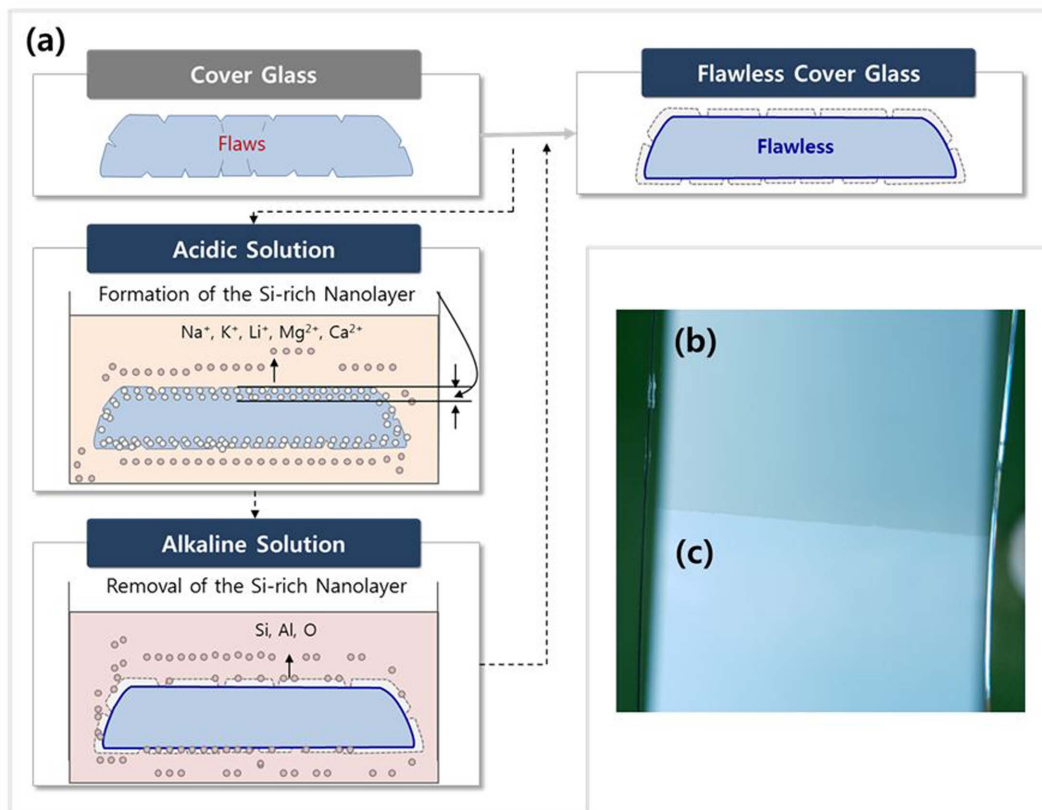


Fig. 1. (a) Leaching process to form and remove the Si-rich Nanolayer (including flaws), (b) top view of glass surface (Si-rich Nanolayer) after soaking in acidic solution, (c) top view of glass surface (Pristine surface) after soaking in acidic and alkaline solution.

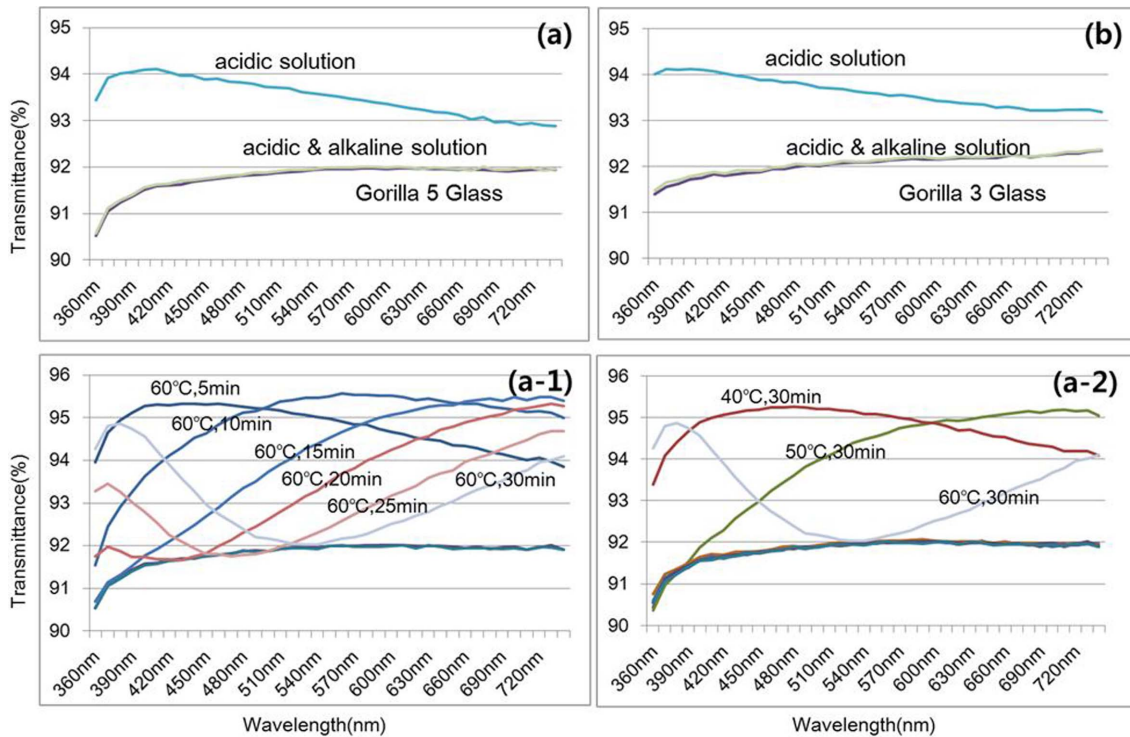


Fig. 2. Comparison of transmittance (a,b) of Gorilla 5 & 3 glass samples after exposing the glass samples to an aqueous acid solution and alkaline solution respectively, transmittance variation as a function of soaking time (c) and temperature (d) in acidic solution.

formation of silica-rich nanolayer, half of the sample of glass was sealed with masking tape after exposure to an acidic solution followed by an alkaline solution soak. Figure 1 (b, c) shows the top view of glass surface before and after alkaline solution exposure. Fig. 1(b) indicates the silica-rich layer formed on the glass surface after soaking it with an acidic solution, and Figure 1(c) shows the silica-rich layer was removed with an alkaline solution.

Transmittance spectra of the Gorilla 3 & 4 glass samples are presented in Fig. 2(a, b) respectively. Both glass samples show transmittance increase after exposure to an acidic solution due to the formation of silica-rich nanolayer which is a relatively low density that reduces the reflectance. The transmittance quickly recovered to a pristine state by removing the silica-rich nanolayer in an alkaline solution. Fig. 2(a-1, a-2) shows the time and temperature dependence of the silica-rich nanolayer. The maximum transmittance point moving to high wavelength means that the silica-rich nanolayer is getting thicker with the increase of time. The results indicate that temperature and time are important factors in determining the thickness of the silica-rich nanolayer, and the glass samples with relatively thick silica-rich nanolayer easily return to a pristine surface after exposure to an alkaline solution.

The measurements at the borderline were carried out with the same samples in Fig. 1(b, c). As shown in Fig. 3(a), AFM indicates 268 nm as the thickness of the silica-rich nanolayer and this value was confirmed with

LCM measurement at 8 points. Mechanical impact with a steel ball made the silica-rich nanolayer separate. As seen in Fig. 3(c, c-1, c-2), approximately 635 nm thick silica-rich layer was separated successfully, and the removed surface was as flat as pristine glass.

The glass compositions in the silica-rich layer were analyzed with TEM EDS mapping and shown in Fig. 4. The results indicate that the silica-rich layer consists of Si and O ions and Na and K ions were leached out to a certain depth. It is confirmed again that the silicon-rich layer was completely removed after exposure to an alkaline solution.

In order to prove the effect of the leaching process on the mechanical strength of glass, the silica-rich nanolayer with a thickness of 300~400 nm was formed by exposing the sample to an acidic solution and removed by dipping the sample in an alkaline solution. To measure the glass surface strength before and after the leaching process, ball drop testing was conducted by impacting the center of the glass surface with a 150 g steel ball. Height was increased at intervals of 5 cm until the breaking point was found. The results are presented with a Weibull plot as seen in Fig. 5. In terms of the scale parameter of 63.2%, it is clear that the surface is strengthened as the leaching process increases 1.9 times. The more interesting point is that the surface quality was as good as pristine glass and there was no known side effects caused by this process.

In this study, glass leaching was introduced to improve mechanical property of chemically strengthened

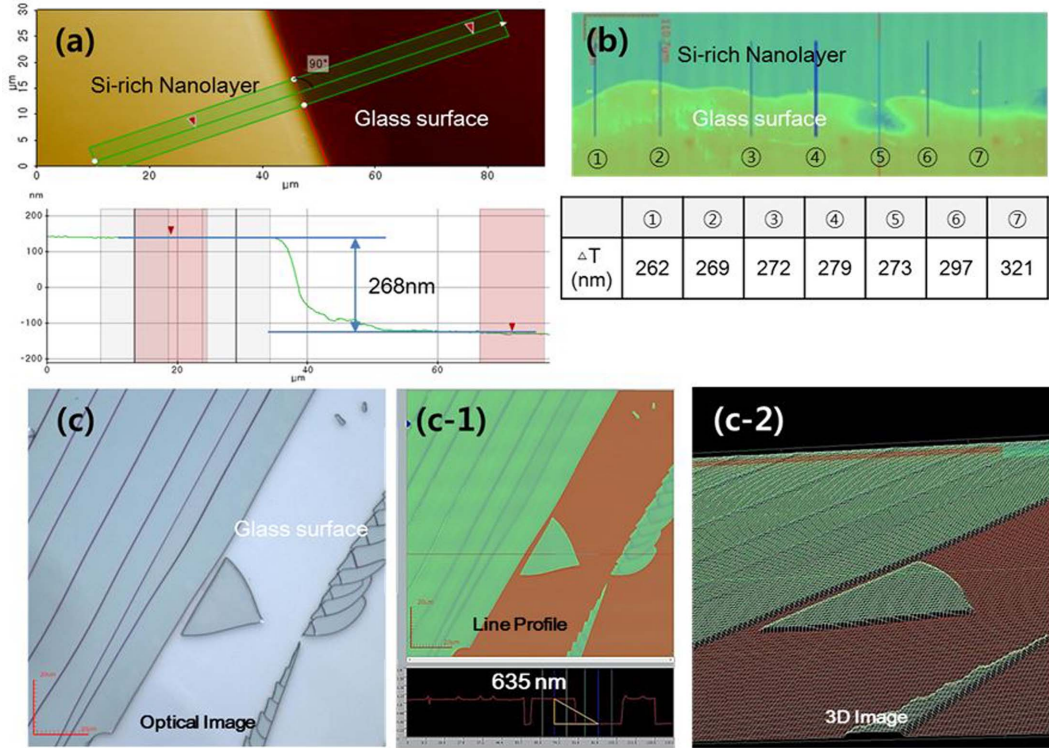


Fig. 3. Thickness of silica-rich nanolayer at the boundary (a) with AFM analysis and (b) with LCM analysis, (c) uniformity after removal of silica-rich nanolayer.

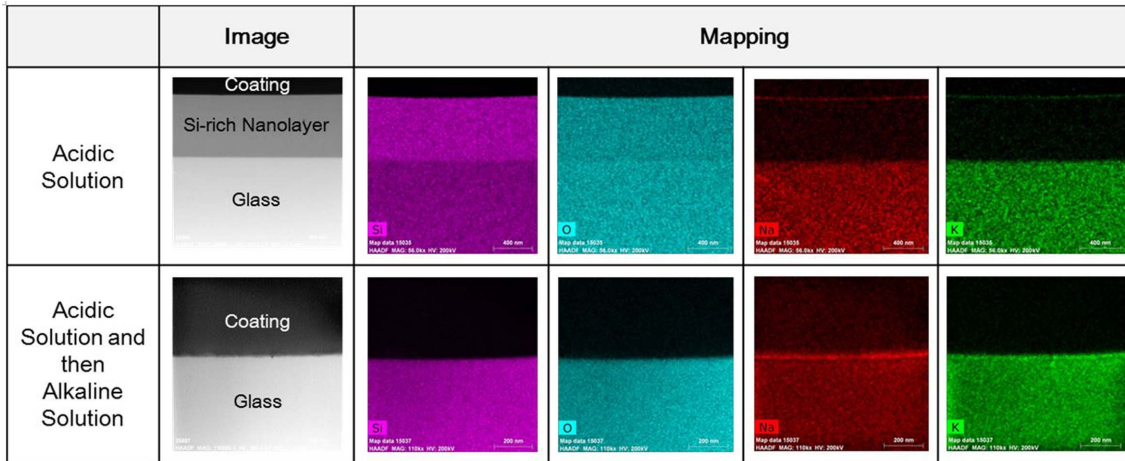


Fig. 4. TEM EDS mapping on fractured glass surface as a function of the chemical cleaning process.

glass. A silica-rich layer that reached flaw depths was formed on the surface of the glass by exposing the glass to an acidic solution. The thickness of silica-rich layer was controllable by adjusting the time and temperature of the solution. The formation of a silica-rich layer was confirmed with naked eye, and the thickness was measured by AFM and LCM. TEM mapping revealed that the silica-rich layer was composed of Si & O, and the layer was removed completely after being soaked in an alkaline solution.

In order to see the effect of the leaching process on

glass surface strength, a ball drop test was performed with a 150 g steel ball. The glass strength increased with the thickness of silica-rich layer and saturated at 300 nm. When the silica-rich layer was thicker than 1000 μm , the glass strength was decreased due to the loss of compressive stress. The saturation point was selected in the range of 300~400 nm, and the reduction of compressive stress was 30~40 MPa. An interesting point is that this method doesn't have trade off among the strength, surface quality, hardness and long-term reliability. This work will serve as a foundation for

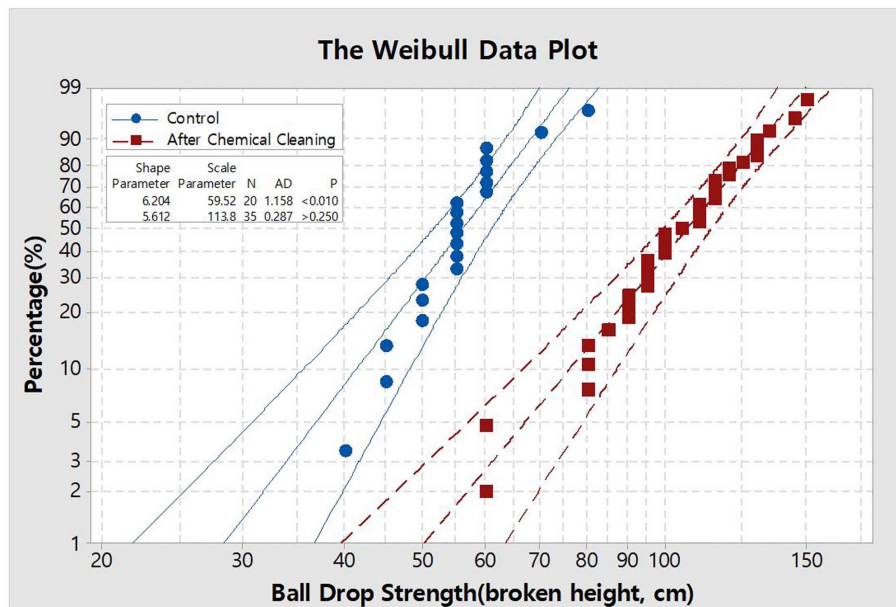


Fig. 5. Weibull plots for data sets of ball drop strength with 150 g steel ball; 95% confidence intervals.

mending surface flaws in ion-exchanged glass.

Conclusions

Leaching of glass made the silica-rich nano layer on ion-exchanged glass, and removed it as well. The thickness of the silica-rich layer was varied as a function of the glass soaking time and the temperature of the acidic solution within the range of 100 nm ~1500 nm. The alkaline solution caused the glass to have a pristine surface by removing the silica-rich layer composed of Si and O. We also demonstrated that leaching can improve the strength of ion-exchanged glass dramatically (up to two times the original strength) without any degradation of surface quality.

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