

Chemical Strengthening Involving Outward Diffusion Process of Na⁺ Ion in Iron-containing Soda-lime Silicate Glass

Hyun-Bin Choi and Eun-Tae Kang[†]

School of Nano & Advanced Materials Engineering, Engineering Research Institute, Gyeongsang National University, Jinju 660-701, Korea

(Received January 20, 2015; Revised February 6, 2015; Accepted February 12, 2015)

ABSTRACT

The outward diffusion of Na⁺ ions in iron-bearing soda lime silicate glass via oxidation heat treatment before the ion exchange process is artificially induced in order to increase the amount of ions exchanged during the ion exchange process. The effect of the addition process is analyzed through measuring the bending strength, the weight change, and the inter-diffusion coefficient after the ion exchange process. The glass strength is increased when the outward diffusion of Na⁺ ions via oxidation heat treatment before the ion exchange process is added. For the glass subjected to the additional process, the weight change and diffusion depth increase compared with the glass not subjected to the process. The interdiffusion coefficient is also slightly increased as a result of the additional process.

Key words : Ion-exchange, Chemical strengthening, Soda-lime silicate glass, Oxidation heat-treatment

1. Introduction

Although there are several methods of strengthening glasses, chemical strengthening method by ion-exchange has several advantages such as being able not only to strengthen 0.5 mm-thick glasses thinner than the minimum glass thickness of 5 mm to which physical strengthening method can be applied but also to increase the strength and being applicable to glasses irrespective of their shapes.¹⁾ Whereas physical strengthening method can be applied to most glasses, chemical strengthening method is applied only to particular glass compositions where ion-exchange is easy and has a high unit production cost. While the scope of application for chemically strengthened glasses is very wide, the most frequently used production areas for commercial purpose include display panels for LCD or AMOLED. These glasses have alkaline aluminosilicate-based compositions known for the highest diffusion coefficient of alkali ions.^{2,3)} On the other hand, soda-lime-silica glass as a representative glass composition system has problems where diffusion rates of Na⁺ ions are slow, depths of generated compressive stress layer are less than 50 μm, while deeper permeation of K⁺ ions relax surface compressive stresses to reduce strengthening effects.⁴⁾

Meanwhile, glass surfaces can be modified by oxidation/reduction reactions. Barton and Billy⁵⁾ have discovered that Na⁺ ions are increased on the surface by oxidation of Cu⁺ ions to Cu²⁺ when flint glass containing 0.4% of copper is

heated in air. Many studies on silicate glasses containing iron⁶⁻¹¹⁾ have also shown that glass-modifying ions due to oxidation of Fe²⁺ ions are diffused from inside to the surface when heat treated near the glass transition temperature in an oxidizing atmosphere. These studies have presented an oxidation mechanism where oxidation of a glass causes diffusion of modifying ions in the opposite direction for charge compensation which results from an inward flux of electron holes rather than supplying oxygen ions to the glass. Based on this, it can be seen that distribution of modifying ions may be artificially controlled in the case of glasses containing transition metal ions having a variety of ionic valencies. By applying this principle, Kang *et al.*^{12,13)} have shown that surfaces of a bio-inert glass can be reformed to bio-active surfaces.

To improve strengths through chemical strengthening by ion-exchange, there should be a high content of alkali ions that are easy to move within the glass, and composition ratios should also be considered to facilitate diffusion of alkali ions. In the case of soda-lime-silicate glasses, for instance, the amounts of ion-exchange are known to be decreased as CaO content is increased.¹⁴⁾ If surface concentrations of Na⁺ ions of a soda-lime-silicate glass can be artificially increased, i.e., the ratios of Na⁺/Ca²⁺ can be increased, then strengths may be improved further by increasing the amounts of ion-exchange even for glasses of a given composition. In the present study, it has been investigated whether the amounts of ion-exchange are actually increased and improvement of strengths is observed by inducing surface diffusion of Na⁺ ions as a result of oxidation heat treatment for soda-lime-silicate glasses of a given composition.

[†]Corresponding author : Eun Tae Kang
E-mail : etkang@gsnu.ac.kr
Tel : +82-55-772-1681 Fax : +82-55-772-1689

2. Experimental Procedure

In the present experiments, strengthening effects were divided for comparison into before and after oxidation heat treatment. Accordingly, some conditions were fixed to reduce variables for effective comparisons. First, the glass as an experiment object was fixed to be of 55SiO₂-14.67Na₂O-29.33CaO-1FeO(mol%) composition. Also, to clarify the effects of oxidation heat treatment, division was made into two groups including the case with oxidation heat treatment and the case without, while ion-exchange was conducted in a molten bath of KNO₃ for 4 h, 5.5 h, 7 h, 8.5 h, 10 h with both groups.

For preparation of glasses, Na₂CO₃ (Aldrich, 99.0%), CaCO₃ (Aldrich, 99.0%), SiO₂ (Junsei), and Fe (C₂O₄) 2H₂O (Aldrich, 99.0%) were weighed respectively to match the composition, and batches were completed by drying after magnetic agitation in ethanol for 3 h. Dried samples were then melted by maintaining for 4 h in a Pt-Rh crucible after temperature rise to 1550°C at a heating rate of 5°C/min. Molten glass were formed in a forming mold made of copper, and slowly cooled in a electric furnace after being maintained for 2 h near the glass transition temperature simultaneously with forming.

Glass transition temperature (T_g) was measured in Air atmosphere at a heating rate of 5°C/min by using a thermal analysis system of Q 600 model by TA instruments company.

The oxidation treatment was conducted in an electric furnace under a flow of O₂/N₂ gas with a fixed oxygen partial pressure of 0.05 atm in order to prevent all Fe²⁺ ions from being oxidized before the modifier ions start to diffuse. The glasses heated at 660°C for 10 h and then were cooled slowly down to a temperature near 100°C in the furnace following heat treatment while the same partial pressure was being maintained. The oxygen partial pressure in the furnace was monitored via a flow-through stabilized zirconia electrolyte sensor that operates at 750°C in a separate furnace downstream of the reaction furnace.

For ion-exchange, the samples were maintained for a set time while being immersed in a molten bath of KNO₃ (Aldrich, 99.0%) in a stainless steel container maintained at 500°C, after which the stainless steel net was recovered and moved to an electric furnace set at 200°C for slow cooling to room temperature to reduce thermal shock at room temperature.

To check how much the strength values were increased after strengthening along with weight changes as a result of ion-exchange between Na⁺ and K⁺. 3-point bending strengths were measured. Weight changes were measured following ion-exchange in the molten salt for a set time, and strengths were measured as a 3-point bending strength by using an apparatus of LR 30K model by LLOYD company. Specimens were produced to be square rods of 3 × 2 × 40 (mm) in size, and measurement values were shown by an estimate of true value at 95% confidence calculated for 6-10 ea of speci-

mens. Also, concentration distributions of Na⁺ ions and K⁺ ions were measured by using EDS(Energy Dispersive X-ray) of 7412 model by OXFORD instements company mounted on SEM (Scanning Electron Microscopy).

3. Results and Discussion

Measured results of bending strength are shown in Fig. 1. Whereas a strength of 73 MPa was indicated in the case of glasses without ion-exchange, strength values for glasses with only ion-exchange without oxidation heat treatment were shown to be 262 MPa in the case of ion-exchange for 4 h, 280 MPa in the case of ion-exchange for 7 h, and 305 MPa in the case of ion-exchange for 10 h. After chemical strengthening by ion-exchange, an increase in strength values by more than 3 times could be affirmed in comparison with the base material.

Also, the glasses with chemical strengthening by ion-exchange after oxidation heat treatment showed strength values of 309 MPa in the case of ion-exchange for 4 h, 345 MPa in the case of ion-exchange for 7 h, and 377 MPa in the case of ion-exchange for 10 h. As clearly shown in Fig. 1, strength values for the glasses with oxidation heat treatment were increased by about 1.2 times as compared with the glasses with only ion-exchange without such pretreatment irrespective of times maintained in the molten salt of KNO₃. And, as the ion-exchange times are increased, strength values were also increased by a small amount, while the glasses with ion-exchange for 4 h after oxidation heat treatment showed a somewhat higher strength than the glasses with only ion-exchange for 10 h. Based on this, it seems reasonable to conclude that the ancillary process of oxidation heat treatment has very positive effects on an increase in strengths of the glasses with ion-exchange.

Figure 2 shows the weight increases after ion-exchange as a function of the square root of time in the case with oxidation heat treatment having been conducted and the case

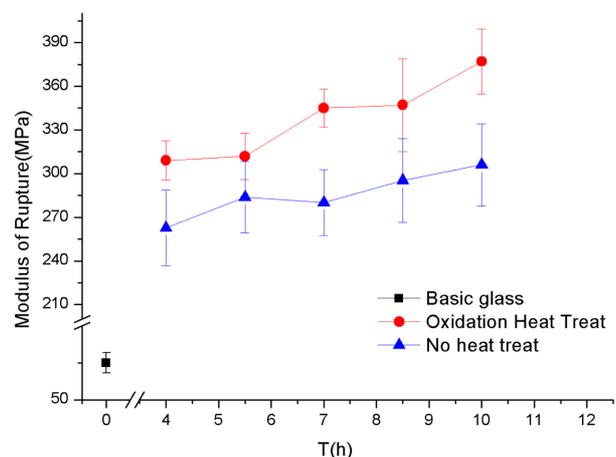


Fig. 1. Modulus of rupture of the mother glass, the heat-treated glass in oxygen atmosphere and the untreated glass with the ion-exchange time.

without. While a linear dependence on \sqrt{t} is observed in the case of only ion-exchange being conducted in the molten salt of KNO₃ without oxidation heat treatment, a dependence on t is observed in the case of oxidation heat treatment being conducted. This suggests that ion-exchange occurs by diffusion and concentrations of diffusing species on the surface are constant in the case without oxidation heat treatment, whereas concentrations of diffusing species on the surface are varied with time as diffusion and surface reaction occur simultaneously in the case of ion-exchange after oxidation heat treatment. Such difference is considered attributable to the fact that outward diffusion of Na⁺ ions in the glass also occurs in the process of ion-exchange in the molten salt in the case of oxidation heat treatment having been conducted. EDS analysis results for the amounts of K⁺ down to an inside depth of approximately 20 μm from the glass surface are shown in Fig. 3. The amounts of K⁺ for the case

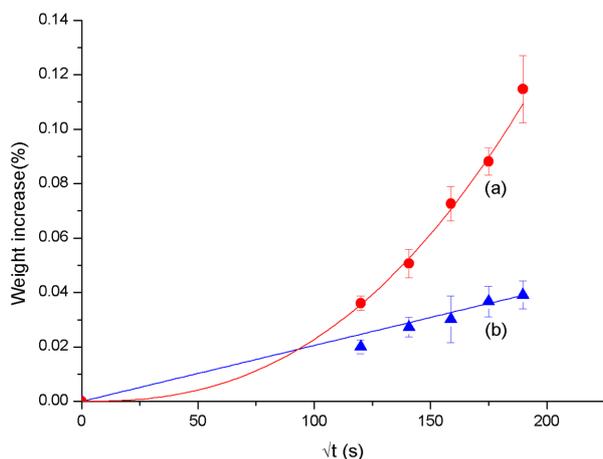


Fig. 2. Relative increase of weight of strengthened glasses as a function of squared root of ion-exchange time (a) heat-treated glass in oxygen atmosphere and (b) untreated glass.

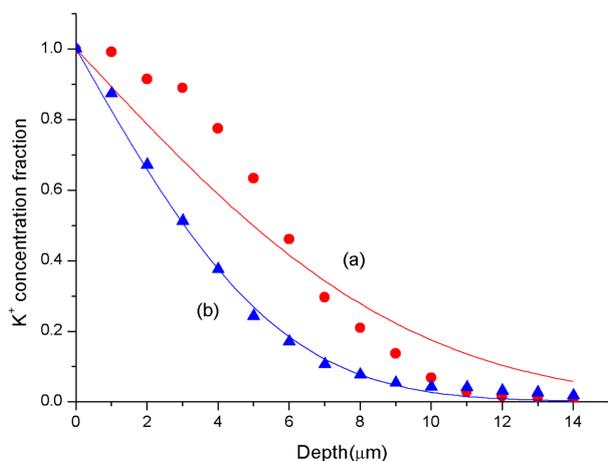


Fig. 3. Potassium concentration profile after 10 h treatment in molten KNO₃ for (a) heat-treated glass in oxygen atmosphere and (b) untreated glass. The solid lines represent the fitting curve determined by Eq. (1).

with oxidation heat treatment are greater than those for the case without by approximately 1~2.5 mol%. Also, whereas K⁺ is affirmed to exist down to about 13 μm in the case of the specimens without oxidation heat treatment, K⁺ could be affirmed to show a deeper diffusion depth down to near 20 μm in the case of the specimens with oxidation heat treatment. This result also demonstrates that the ancillary process of oxidation heat treatment makes a positive contribution to the exchange between Na⁺ ions and K⁺ ions.

Concentration profile $C(x,t)$ of K⁺ ions resulting from diffusion can be given by the equation (1).¹⁵⁾

$$\frac{c(x,t)}{c_0} = \operatorname{erfc}\left(\frac{x}{\sqrt{2Dt}}\right) = 1 - \operatorname{erf}\left(\frac{x}{\sqrt{2Dt}}\right) \quad (1)$$

where C_0 is the initial concentration of the glass surface, x the depth, t the processing time and D the interdiffusion coefficient. Concentration distribution of alkali ions within a glass after mutual diffusion is known not to follow the equation (1).¹⁶⁾ Solid line in Fig. 3 is a line calculated by the equation (1), showing that the concentration profile fails to properly follow the shape of *erfc* for the equation. A more complicated model is required for an accurate description on diffusion. Since interdiffusion coefficients in ion-exchange glasses are known to somewhat depend on concentrations¹⁷⁻¹⁹⁾, the concentration-dependent interdiffusion coefficient \tilde{D} can be calculated in accordance with the Boltzmann-Matano approach²⁰⁾:

$$\tilde{D}(c) = -\frac{1}{2t} \frac{dx}{dc} \int_0^c xdc \quad (2)$$

Since the integration term can have much error in both end portions of the concentration profile curve upon calculation of interdiffusion coefficients by using this equation, compositions for intermediate domains have been calculated. The interdiffusion coefficient calculated from this equation is shown in Fig. 4. The obtained interdiffusion coefficient agrees well with the values reported for soda-lime glasses^{18, 19)}. As indicated in the figure, the value is 1.04×10^{-9} m²/s in average for the case where oxidation heat treatment is conducted before ion-

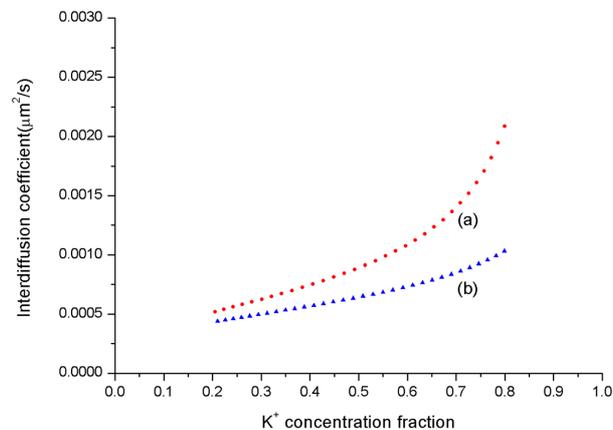


Fig. 4. Potassium interdiffusion coefficient in the ion-exchanged glasses: (a) heat-treated glass in oxygen atmosphere and (b) untreated glass.

exchange, and $6.72 \times 10^{-10} \text{ m}^2/\text{s}$ in the case without the treatment, indicating that the ancillary heat treatment increases chemical diffusion coefficients. From these results, a clear conclusion can be made that the oxidation heat treatment can further improve chemical strengthening by augmenting the amounts of ion-exchange.

4. Conclusion

By heat treatment of soda-lime glasses containing iron in an oxidizing atmosphere to cause outward diffusion of Na^+ ions in the glass, an attempt has been made to augment the amounts of ions exchanged $\text{Na}^+ - \text{K}^+$. In the case of oxidation heat treatment being conducted before ion-exchange, bend strengths, amounts of ion-exchange and diffusion depths could be seen to be increased as compared with the case without undergoing this heat treatment process. In addition, interdiffusion coefficients also showed an increase to a value slightly less than twice. These facts clearly show that the ancillary oxidation heat treatment before ion-exchange can further improve chemical strengthening by augmenting the amounts of ion-exchange by diffusion.

REFERENCES

1. S. Karlsson, B. Jonson, and C. Stalhanske, "The Technology of Chemical Glass Strengthening-A Review," *Eur. J. Glass Sci. Technol. A*, **51** [2] 41-54 (2010).
2. A. J. Burggraaf and J. Cornelissen, "The Strengthening of Glass by Ion Exchange. Part I. Stress Formation by Ion Diffusion in Alkali Aluminosilicate Glass," *Phys. Chem. Glasses*, **5** [5] 123-29 (1964).
3. M. Y. M. Lee, "Glass Part 3: New Generation of Specialty Glass for LCDs and AMOLEDs," *Gases & Instrum.*, March/April 1-6 (2013).
4. A. K. Varshneya and P. Kreski, *The Chemistry of Chemical Strengthening of Glass in Processing, Properties, and Applications of Glass and Optical Materials*; pp. 107-12 in *Ceramic Transactions Vol. 231*, Ed. by A. K. Varshneya, H. A. Schaeffer, K. A. Richardson, M. Wightman, L. D. Pye, John Wiley & Sons, Inc., Hoboken, New Jersey, 2012.
5. J. L. Barton and M. D. E. Billy, "Diffusion and Oxidation of Cu^+ in Glass," *J. Non-Cryst. Solids*, **38&39** 523-26 (1980).
6. G. B. Cook, R. F. Cooper, and T. Wu, "Chemical Diffusion and Crystalline Nucleation During Oxidation of Ferrous Iron-bearing Magnesium Aluminosilicate Glass," *J. Non-Cryst. Solids*, **120** 207-22 (1990).
7. R. F. Cooper, J. B. Faselow, and D. B. Poker, "The Mechanism of Oxidation of a Basaltic Glass: Chemical Diffusion of Network-Modifying Cations," *Geochim. Cosmochim. Acta*, **60** 3253-65 (1996).
8. D. R. Smith and R. F. Cooper, "Dynamic Oxidation of a Fe^{2+} -Bearing Calcium-magnesium-aluminosilicate Glass: The Effect of Molecular Structure on Chemical Diffusion and Reaction Morphology," *J. Non-Cryst. Solids*, **278** [1-3] 145-63 (2000).
9. G. B. Cook and R. F. Cooper, "Iron Concentration & the Physical Processes of Dynamic Oxidation in an Alkaline Earth Aluminosilicate Glass," *Am. Mineral*, **85** [3-4] 397-406 (2000).
10. V. Magnien, D. R. Neuville, L. Cormier, J. Roux, J. L. Hazemann, D. de Ligny, S. Pascarelli, I. Vickridge, O. Pinet, and P. Richet, "Kinetics and Mechanisms of Iron Redox Reactions in Silicate Melts: The Effects of Temperature and Alkali Cations," *Geochim. Cosmochim. Acta*, **72** [8] 2157-68 (2008).
11. M. M. Smedskjaer and Y. Yue, "Inward and Outward Diffusion of Modifying Ions and Its Impact on the Properties of Glasses and Glass-Ceramics," *Int. J. Appl. Glass Sci.*, **2** [2] 117-28 (2011).
12. E. T. Kang and J. P. Kim, "Conversion from a Bio-inert Glass to a Glass with Bio-active Layer by Heat-treatment in an Oxidation Atmosphere," *Phys. Proc.*, **48** 46-54 (2013).
13. E. T. Kang, J. P. Kim, and C. Y. Kim, "Surface Modification and Bio-activation of Bio-inert Glasses through Thermal Oxidation," *J. Non-Cryst. Solids*, **389** 1-10 (2014).
14. M. E. Nordberg, E. L. Mochel, H. M. Garfinkel, and J. S. Olcott, "Strengthening by Ion Exchange," *J. Am. Ceram. Soc.*, **47** [5] 215-19 (1964).
15. P. G. Shewmon, *Diffusion in Solids*; pp. 22, McGraw-Hill, New York, NY, 1991.
16. R. Gy, "Ion Exchange for Glass Strengthening," *Mat. Sci. Eng. B*, **149** [2] 159-65 (2008).
17. A. K. Varshneya and M. E. Milberg, "Ion Exchange in Sodium Borosilicate Glasses," *J. Am. Ceram. Soc.*, **57** [4] 165-69 (1974).
18. J. Shen, D. J. Green, and C. G. Pantano, "Control of Concentration Profiles in Two Step Ion Exchanged Glasses," *Phys. Chem. Glasses*, **44** [4] 284-92 (2003).
19. L. Jiang, X. Guo, X. Li, L. Li, G. Zhang, and Y. Yan, "Different $\text{K}^+ - \text{Na}^+$ Inter-diffusion Kinetics between the Air Side and Tin Side of an Ion-exchanged Float Aluminosilicate Glass," *Appl. Surf. Sci.*, **265** 889-94 (2013).
20. J. Crank, *The Mathematics of Diffusion*; pp. 230-34, Clarendon press, Oxford, UK 1975.