Journal of Information Display, vol. 4, no. 3, 2003

Improvement of Mechanical Property by Single Ion Exchange Process in Substrate Glass

Hoi Kwan Lee[a], Won Ho Kang[a], and David J. Green[b]

Abstract

In connection with the ion exchange strengthening on soda-lime-silicate, substrate glass for display use was investigated. In the processing, the temperature was varied during the ion exchange in order to make stress profile and to determine optimum condition. In the present work, we found that the maximum value of strength was 617.8 MPa after an ion exchange process at 470 ℃ for 1h, and then, at 450 ℃ for 24h. Also, the effect of residual stress placed on the near surface was measured by analyzing the number of crack branches and brittleness. This approach allowed us the residual stress profile to be engineered to improve mechanical reliability.

Keywords : ion exchange, chemical strengthening, strength, fractography

1. Introduction

Glass has a unique combination of desirable properties for various engineering applications, such as transparency, hardness, durability and low cost. The problem is that glass exhibits brittle fracture and is can be easily damaged, which in turn leads to low strengths and design stresses. Ion exchange is one approach to solve this problem and has been studied for the past four decades [1].

Recently, it has been demonstrated that the residual stress profile produced by the ion exchange process can be manipulated to induce crack arrest and multiple cracking, whilst maintaining significant level of strengthe and very little variability [2,3]. In this study, the stress profile was manipulated by using the two-step exchange process. In the first step, potassium ions were exchanged for sodium ions in the glass surface in a traditional fashion in the molten potassium nitrate. In the second step, the sample was immersed into a molten mixture of potassium and sodium nitrates in which a fraction of the sodium ions were exchanged for potassium in order to make residual compression to be slightly below the surface. This approach allows the position of the maximum compression and the stress gradients to be controlled. Currently, a variable temperature ion exchange process has been introduced [4]. This approach allows control over shape of the residual stress profile. However, although the processing is effective to in terms of improving glass strength, it requires the use of two kinds of molten solution namely as sodium nitrates and mixture of sodium and potassium nitrates, there by causing the procedure to be less economically attractive.

In this study, a single ion exchange process was suggested in order to simplify the procedure, and the temperature was varied during the ion exchange to make stress profile.

2. Experimental Procedure

Soda-lime-silicate (Glass code AS, AGC, Japan) glass substrates for LCD were used to produce

---

Manuscript received May 9, 2003; accepted for publication June 23, 2003.

Corresponding Author : Hoi Kwan Lee
a. Department of New Materials Science and Engineering, Dankook University, San 29, Anseo-dong, Cheonan-city, Choongnam 330-714, Korea.
b. Department of Materials Science and Engineering, The Pennsylvania State University, University park, PA 16802, USA.
E-mail : hoikwanlee@korea.com, **Tel** : +41 550-1816 **Fax** : +41 550-3530

strengthened glasses by single ion exchange process. The chemical composition of the glass is given in Table 1. For the strength testing, the glass was cut into beams with rectangular cross sections; nominal size of 1.1 X 8X70 mm. The samples were chamfered using SiC paper and polished with CeO_2 powder to remove corner flaws. The glass bars were annealed at 560℃ for 8h in air in order to remove residual stresses associated with the machining. The ion exchange was performed using a semiautomatic furnace, which was equipped with such devices such as stainless steel bath, cooling fan and stirrer motor. In the procedure, the single ion exchange was performed in molten KNO_3. During the processing, the temperature was first set to as high as 470-560 ℃ between (0.5 and 4h). The temperature was then reduced to 450 ℃ for 24h, which is typical for a normal ion exchange process. The strength was measured by three-point bending (cross head speed: 7.5 mm/mim, load span: 30mm). After each bending test, the fractured samples were observed in an optical microscope in order to observe failure surfaces. Finally, the fracture toughness of the ion-exchanged glass was measured using a Vicker's hardness indenter based on the approach suggested by Evans and Charles [5].

Table 1. Chemical composition of soda lime silicate glass (wt%)

SiO_2	Al_2O_3	RO	Na_2O
72.5	2	12	13.5

3. Results and Discussion

3.1 Strength of SLS glass at various temperatures

The strength data for samples treated in fused KNO_3 at temperatures ranging from 470 ℃ to 560℃ for a period from 0.5h to 4h and kept in the same salt at 450℃ for an additional 24h are shown in Fig.1. The strength in the single ion exchanged glass increased by a factor of ~7 from annealed glass prior to exchange (88.3 to 617.8 MPa). The increase in the temperature at the initial stages of the single ion exchange process caused a decrease in glass strength when the second stage for a normal ion exchange was fixed at 450 ℃ for 24h. Such result shows that the strength data depends on the initial stage, and that the higher the initial temperature, the lesser the strength as structural relaxation and self-annealing of samples are accelerated.

Moreover, by increasing the time of this state, the bend strength curve has maximum value except 560 ℃. As a whole, however, the increase in the time at the initial stage causes a decrease in glass strength, and the samples treated for a long ion exchange time have lower strength of much less than sample (435.3 MPa) treated for 450℃ at 24th without initial stage. Such phenomenon is prominent when the temperature and time of the initial stage increase, suggesting that the temperature of the initial stage takes a great effect on this result.

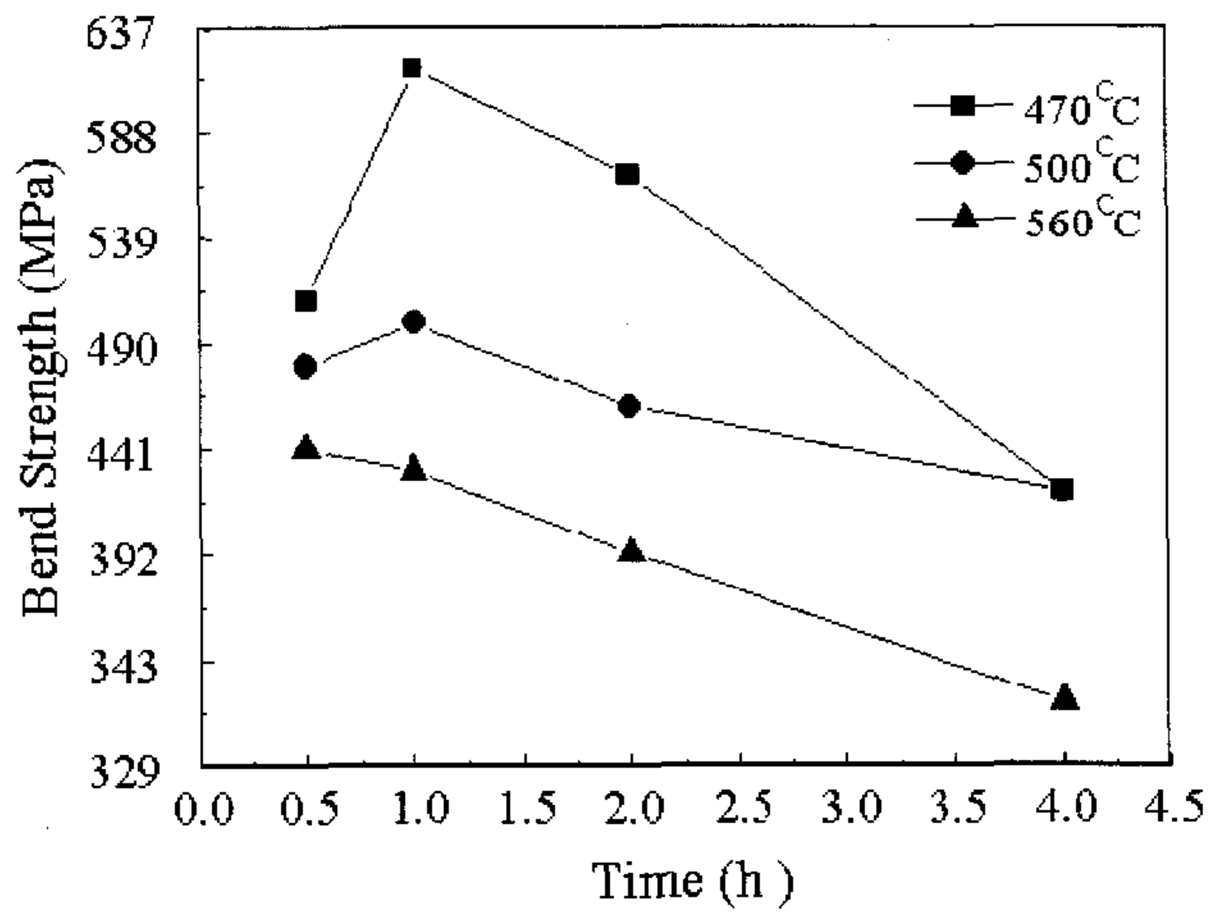

Fig. 1. Bend strength of the ion exchanged specimens as a function of time and temperature in the initial stage of processing.

This phenomenon is considered to be a replacement of sodium ion in [NaOn] polyhedron in the network of the soda-lime silicate glass by potassium ion in molten salt. The is substitution produces a new [KOk] polyhedron surrounded by [SiOm] polyhedron in the network of the glass, and the difference in sizes between potassium ion (2.99 Å) and sodium ion (1.99 Å) causes very high local stresses, developing in [KOk] which is surrounded by [SiOm]. However, when the temperature is high and time of the initial stage is long, those stresses relax rapidly as a result of the breaking of stretched bridging Si-O bonds surrounding [KOk] polyhedron[4]. Therefore, the glasses treated at 470 ℃ and 500 ℃ for a period from 0.5 to 1h show that the strengthening phenomenon was superior to the stress relaxation, and at

Table 2. Fracture Strength Data for the Single Ion Exchanged Glass according to Ion-exchange Time

Temp. (℃)	Time (h) / Properties	0.5	1	2	4
470	Standard Deviation (MPa)	57.83	39.22	60.80	42.17
	Coefficient Variation (%)	11.35	10.32	10.69	10.00
500	Standard Deviation (MPa)	24.52	19.62	34.32	15.68
	Coefficient Variation (%)	5.10	3.92	7.45 0	3.72
560	Standard Deviation (MPa)	60.80	55.89	49.03	17.65
	Coefficient Variation (%)	13.19	12.95	12.50	5.45

the same temperature for the period from 1 to 4 h the stress relaxation caused by self-annealing phenomenon and structural relaxation was superior to the strengthening appearance. For this reason, each temperature had a maximum point in strength. At the temperature of 560℃ however, the strength decreased without a maximum point because the structural relaxation as well as the self-annealing effect were accelerated[3,6]. In order to obtain a glass of higher strength the above-mentioned conditions should be considered.

The above analysis provides an ideal condition to obtain high strength glass. In Table 2, strength variability is qualified in terms of the standard deviation and the coefficient of variation. The ideal condition is shown at 500 ℃ compared with glass without ion exchange process (68.6MPa, 7.8 %). In the precedent experiment, Tandon and Green provided that the standard deviation was increased for all exchange conditions [11], but this experiment did not precisely follow the precedent one. However, the author assumes that the change in the standard deviation and the coefficient was due to the residual stress formed by single ion exchange process. Furthermore, this residual stress placed on near glass surface can be considered to have contributied to the fracture resistance as mentioned by Green and Tandon. Although the strengthening is often combined with a deleterious increase in the coefficient variation in glass strength as measured by the standard deviation in Table 2, it is more important to identify the strength of ion-exchanged glass and increase the reliability in glass strength.

3.2 Fractography study

As an above-mentioned statement, this process produces residual stress slightly below the glass surface, and such stress affects the fracture resistance and glass shards. Fig. 2 shows a glass surface observed through an optical micrographs after bending test that includes cracks [A]. The number of these cracks on the glass surface was not conspicuously changed throughout the various ion exchange conditions. However, crack branches placed below the surface cracks were different from the surface crack in the its number. Fig. 2 [B] is observed at the same place of Fig. 2 [A] when the focus of optical microscope was readjusted into Fig. 2 [A] below. The number of the crack branches showed that it has a relation with the ion exchange condition. More importantly, the above property was not found in union-exchanged glasses, and it was clear that there was a layer-a residual stress between the surface cracks and the crack branches produced by single ion exchange process against the fracture. It can absorb the elastic deformation and produces crack branches compared with its ability to absorb the elastic deformation.

Fig. 3 shows bending strength versus the number of branches events observed for fractured glasses. In these data, the number of the cracks was counted by using the optical microscope of one hundred magnification in Fig. 2, and all observations were carried out evenly according to each condition. The result showed a linear relation between the number of crack branches and the bending strength. In case where the bend strength was increased, the number of branches was also increasd in fractured glasses. On the other hand, the number of branches decreased in decreasing the bend strength. These phenomena demonstrate that the number of crack branches in the glass can reflect its strength and could be controlled by single ion exchange process. Furthermore, this result was also very similar to the experimental result conducted by Frechette and Michalske [8].

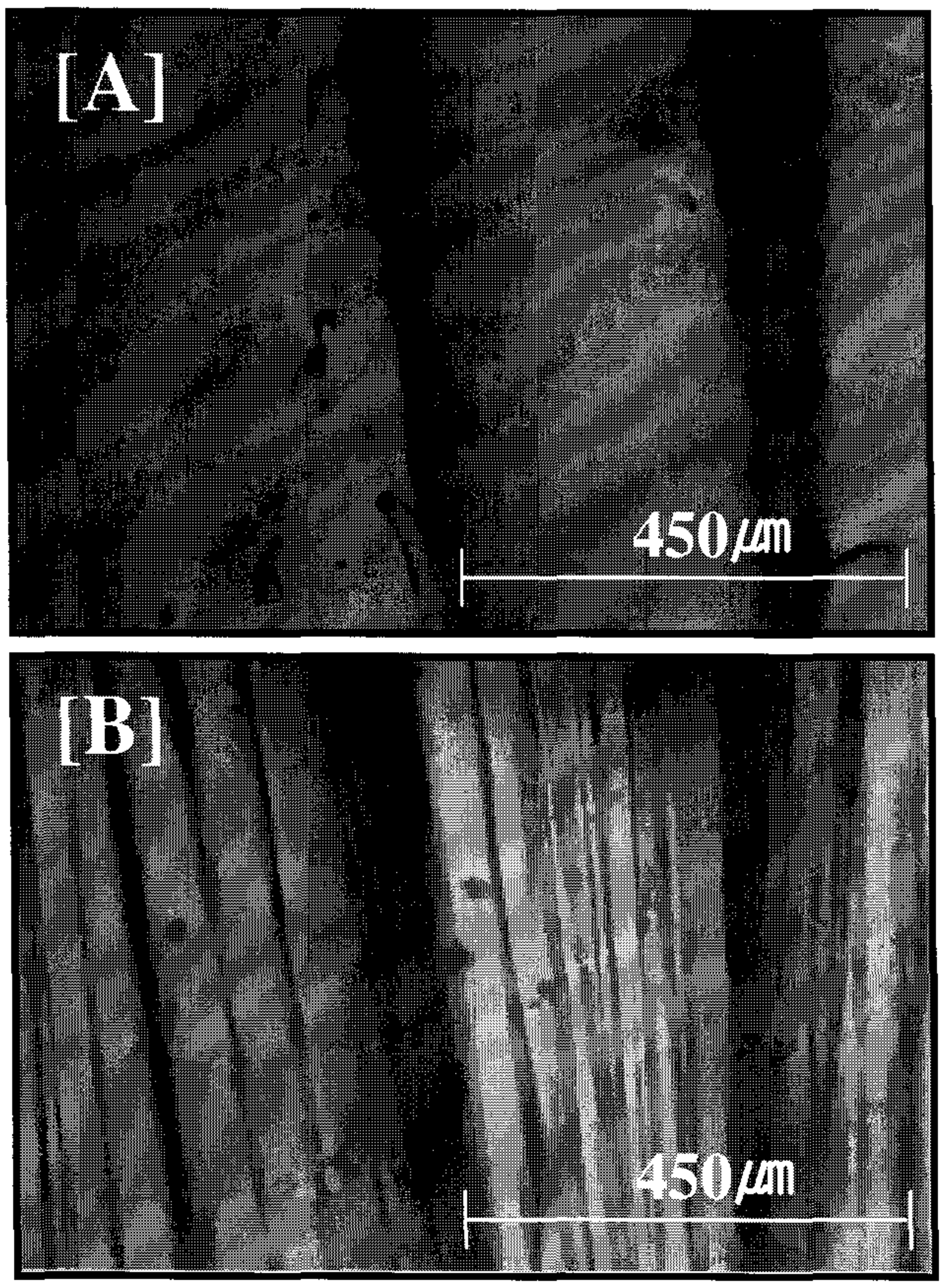

Fig. 2. Optical micrographs of ion exchanged glasses after bending test at 500 ℃ for 1h, 450 ℃ for 24h. (A) surface cracks, (B) multiple crack branches.

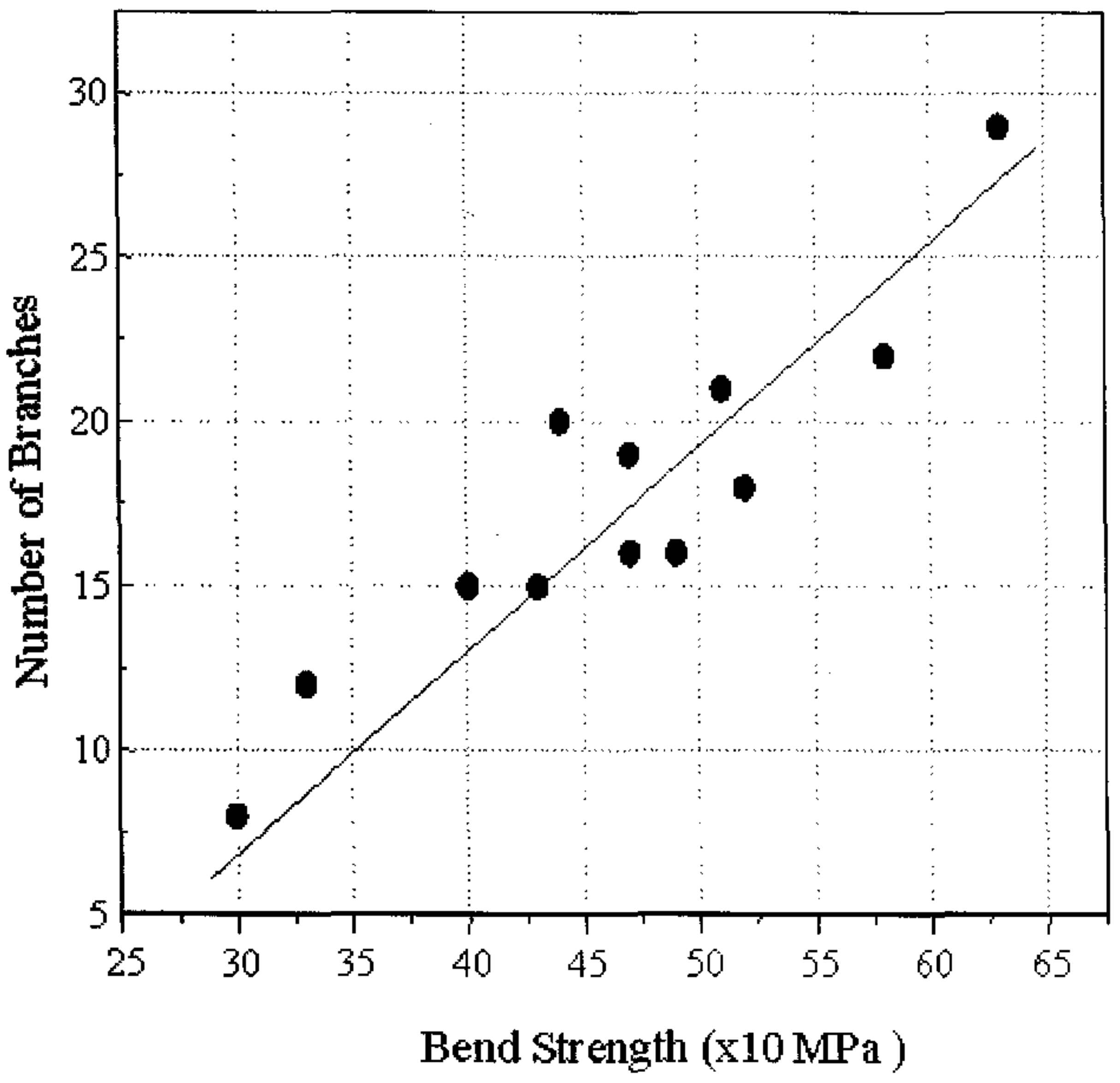

Fig. 3. Bending strength versus the number of branches events observed for fractured glasses.

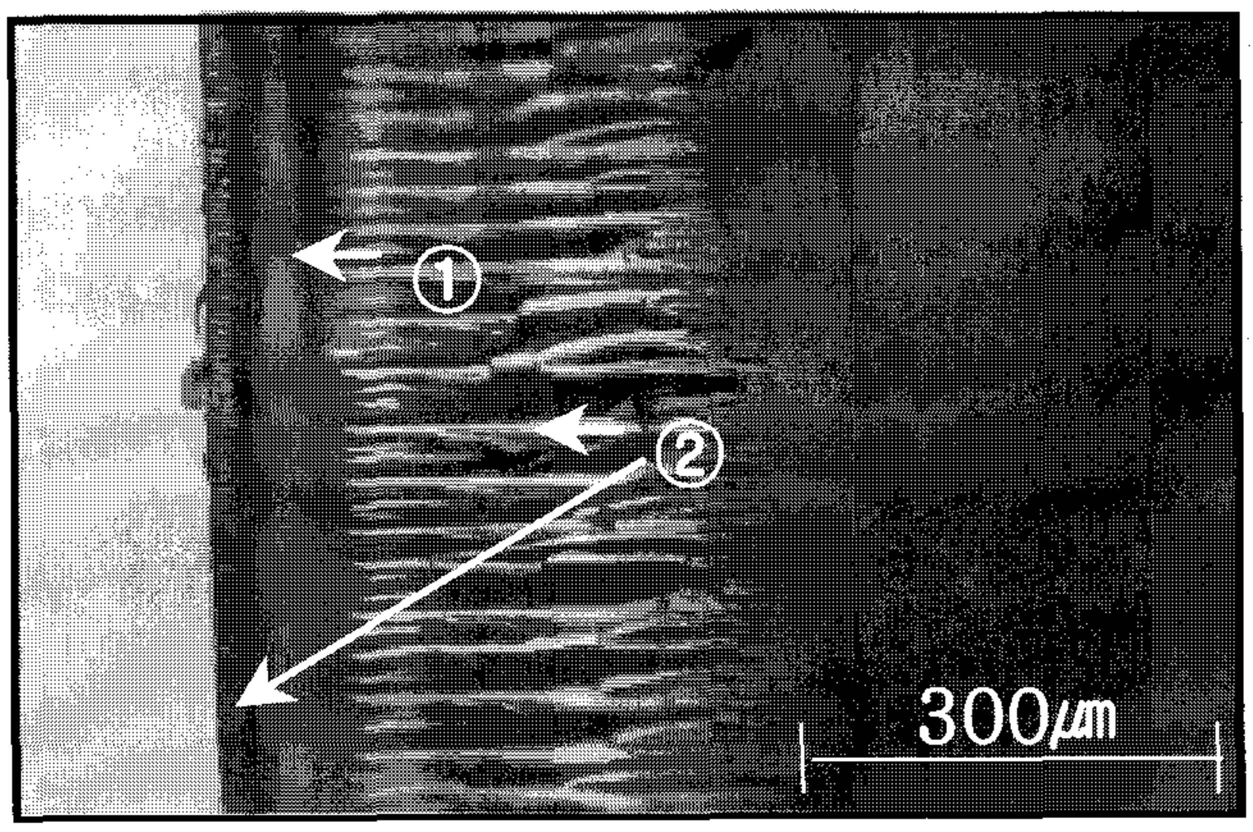

Fig. 4. Fractured surface of ion exchanged glasses after bending test at 500 ℃ for 1, 450 ℃ for 24h. ① is was mirror surface caused by compression stress. ② is hackle region caused by tensile stress.

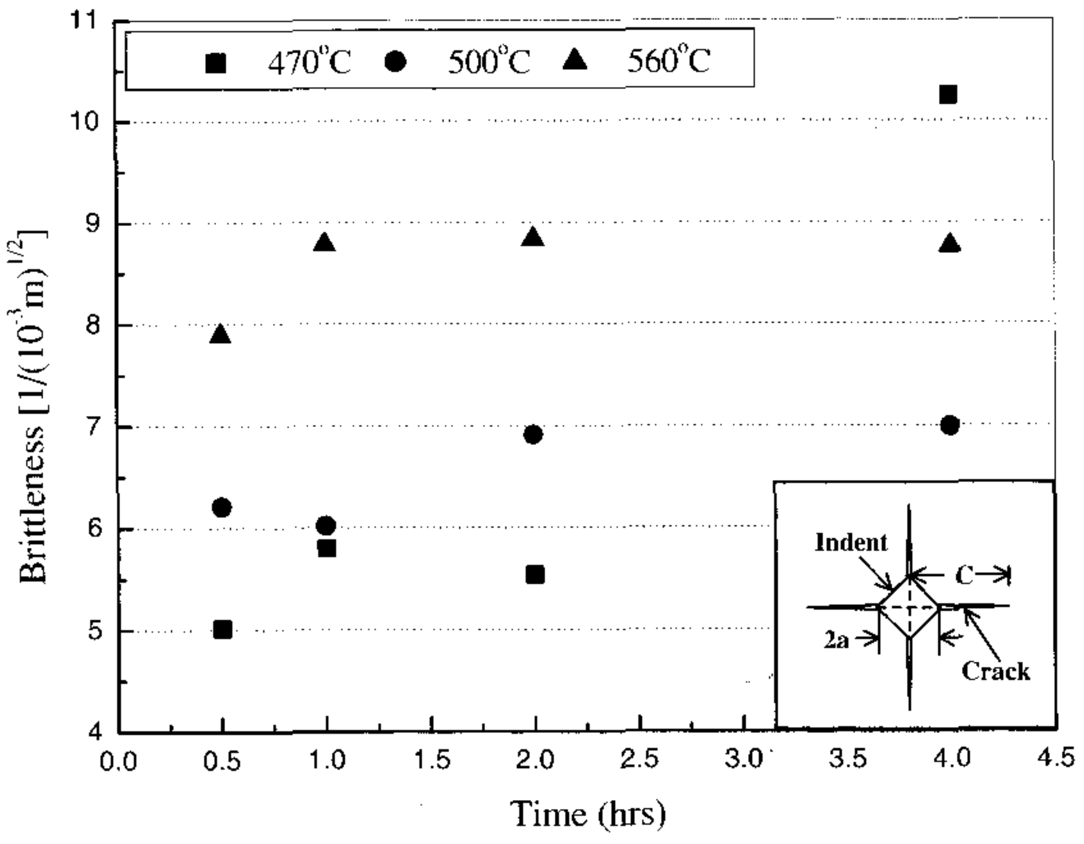

Fig. 5. Brittleness variation according to ion exchange time and temperature. Brittleness of the non-exchanged glass : 13.9 $[1/(10^{-3}\ \mathrm{mm})^{1/2}]$.

In Fig. 2, the author suspected that there are internal residual stresses in ion-exchanged glass, and such stresses make a difference between the cracks and the crack branches as a layer [9]. This assumption is verified by the optical micrograph in Fig. 4. The photographs show a vertical section of the fractured glass after the bending test. These could be divided into two parts such as the ① referred to as mirror area and the ② as hackle near the glass surface [12]. It is known that between residual stress and fracture features, a tensile stress added may increase the rate of crack propagation and accelerate the development of hackle. Alternatively, a compressive stress can be expected to extend parts of the mirror area that may hinder the crack propagation. It was suggested that this dichotomy is caused by single ion exchange process at special condition and consists of both tensile stress and compressive stress. Additionally, the size and interval of hackles were related to the glass strength. For this study, it seems that highest strength specimens have small and dense hackles.

Fig. 5 shows the relation between ion exchange condition and brittleness of glass. At this experiment, the brittleness was measured by using the method conducted by Evans and Charles [5] and Lawn and Marshall [10]. The data shows similarity compared with Fig. 1, except for the brittleness value at 470 ℃ for 4h. The increase in the temperature and time causes an increase in the glass brittleness because of stress relaxation, and in case of the decrease in the time and temperature also the brittleness curve have minimum value. In conclusion, the residual stress caused by single ion exchange process was able to change the glass brittleness even though the brittleness value at 470 ℃ for 4h could not be interpreted clearly until now.

4. Conclusions

We introduced single ion exchange process and changed its condition to make similar stress with current ion exchange process.

1. The maximum value of three-point bending strength was 617.78MPa at 470 ℃ for 1h and kept in the same salt at 450 ℃ for 24h, and the ideal condition of reducing the standard deviation and the coefficient variation of the glass is shown at 500 ℃ for 1h, the values were 19.62 Mpa and 3.92, respectively.
2. The fractography study showed not only that this process produces residual stress near glass surface but also that such stress has some effection with glass strength and crack branches.
3. The residual stress in glass decreases the brittleness by prohibiting crack propagation, and the brittleness value of the ion-exchanged glass decreased by a factor of ~1/3 from annealed glass prior to exchange 13.9 to 5 $[1/(10^{-3}\text{ m})^{1/2}]$. Therefore, conclude that the residual stress by single ion exchange process increases the glass strength and toughness.

References

[1] M. E. Nordberg, E. L. Mochel, H. M. Garfinkel and J. S. Olcott, J. Am. Ceram. Soc., **47,** 215 (1964).

[2] D. J. Green, R. Tandon, and V. M. Sglavo, The American Association for the advancement of Science, **283,** 1295 (1999).

[3] D. I. Lee, Y. K. Lee, and H. S. Lee, J. Kor. Ceram. Soc., **25,** 665 (1988).

[4] V. Belostotsky, J. Non-Cryst. Solids, **238,** 171 (1998).

[5] A. G. Evans and E. A. Charles, J. Am. Ceram. Soc., **59,** 371 (1976).

[6] D. I. Lee, Y. K. Lee, and H. S. Lee and J. Kor. Ceram. Soc., **25,** 237 (1988).

[7] C. K. Lee and I. S. Kim, J. Kor. Ceram. Soc., **24,** 335 (1987).

[8] T. A. Michalske and V. D. Frechette, Bull. Am. Ceram. Soc., **57,** 427 (1978).

[9] M. J. Kerper and T. G. Scuderi, Bull. Am. Ceram. Soc. **44,** 953 (1965).

[10]B. R. Lawn, A. G. Evans, and D. B. Marshall, J. Am. Ceram. Soc., **63,** 571 (1980).

[11]D.J. Green, Z.Metalkd, **90,** 1059 (1999).

[12]S. J. Schneider, Jr. Engineering Materials Handbook, (ASM International, Vol. 4), p.635 (1992).