**Correlation between K^+ - Na^+ diffusion coefficient and flexural strength of
chemically tempered aluminosilicate glass**

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Abstract: The correlation between K^+ - Na^+ diffusion coefficient and mechanical properties of chemically tempered and hybrid tempered (chemically tempered subsequent to thermally tempered) aluminosilicate glass are investigated. Firstly, the potassium ion concentration profiles are experimentally measured and the diffusion coefficient is calculated according to the Boltzmann-Matano approach. Secondly, the flexure strength and Weibull modulus are determined using a combined experimental (coaxial double ring) and finite element analysis method. The results indicate that the flexural strength decreases with the diffusion coefficient of the air side for both types of glass samples while there is no significant relationship between diffusion coefficient and Weibull modulus. Diffusion coefficient on air side shows a higher value than that of the tin side. With the same diffusion coefficient, the flexural

strength of chemically tempered glasses are found to be higher than that for hybrid tempered glasses. The effect of diffusion coefficient on modulus of rupture (MOR) for hybrid tempered glass is more remarkable. These results would be useful in designing the strength of glass and guiding the strengthening process by chemical or hybrid tempering.

Key words: diffusion coefficient; flexural strength; chemically tempered glass; hybrid tempered glass

1. Introduction

Chemical tempering, also known as ion exchange, is a process in which ions of a larger size, compared to those already exist in the glass matrix, are “stuffed” into the glass surface. This generates compressive stresses (CS) on the surface which results in the strengthening of glass [1, 2]. K^+Na^+ ion exchange, which was first raised by Kistler in 1962, is the most commonly used approach of ion exchange [3]. The mechanism of K^+Na^+ ion exchange can be understood as an interdiffusion process and the exchange rate is dependent on the composition, structure and surface conditions of the glass [4]. Understanding the diffusion kinetics of K^+Na^+ ion exchange is of critical importance not only for long-standing fundamental interest [5, 6], but also for controlling the mechanical properties of glasses. Different aspects of the K^+Na^+ interdiffusion process has previously been investigated including: the influence of glass composition, exchange temperature and time on the K^+Na^+ diffusion coefficient [4, 6-8], the impact of different salt bath composition on the kinetics of ion exchange process [9], the diffusion coefficient for two step ion

exchange [10] and the relationship between the diffusion process of K^+ ions and the surface hardness [11, 12]. Recently, the concept of engineered stress profile (ESP) glass is proposed by Green and Sglavo [13-15]. ESP glasses can be produced via a two-step chemical tempering process. The stress profiles of the ESP glasses are specially desired which can lead to strengthening and insensitivity of strength to the initial surface flaw size. The K^+ - Na^+ interdiffusion process, which determines the stress profiles, is very important in controlling the strength of chemically tempered glasses [10]. Therefore, to elucidate the correlation between the K^+ - Na^+ diffusion coefficient and flexural strength of chemically tempered glasses is an important issue in glass-strengthening technology.

Thermal tempering, also known as physical strengthening, is another effective method to strengthening glass. It can produce a deeper layer of CS than chemical tempering technique. However, the magnitude of CS at the surface of thermally tempered specimens is much smaller than that of chemically tempered specimens. A combination procedure of chemical and thermal tempering can have a significant difference from the two methods applied alone [16, 17]. To date, very few studies focus on the strengthening effect of the combined treatment, thermal tempering followed by chemical tempering, on glass or ceramic materials. The correlation between K^+ - Na^+ diffusion coefficient and flexural strength of chemical tempering or chemical tempering subsequent to thermal tempering is still remains unclear.

In addition, approximately 90% of all flat glasses are manufactured using the float forming process in which the molten glass will be immersed into a tin bath [18-20].

During this process, the molten tin ions can diffuse into the glass surface, producing two chemically different sides, which are often referred to as the air and tin sides. The difference in composition and structure between the two sides can lead to different properties [21-23] and diffusion characteristics. The diverse diffusion performance between air and tin sides in chemical tempering subsequent to thermal tempering is still unknown.

The main object of this study is to investigate the correlation between K^+Na^+ diffusion coefficient and flexural strength of chemically and hybrid tempered (chemically tempered subsequent to thermally tempered) specimens. The variation of compressive stress and surface structure are identified to interpret the difference between the two kinds of specimens. Results show that the flexural strength decreases with increasing diffusion coefficient of the air side for both types of glass samples. However, the effect of K^+Na^+ diffusion coefficient on Weibull modulus is more complex than on the flexural strength. In addition, the flexure strength of the chemically tempered glasses is higher than that of the hybrid tempered specimens with the same K^+Na^+ diffusion coefficient.

2. Experimental procedure

2.1 Materials and strengthening process

The glass used in this work is a square plate with an average length of 100.0 ± 0.5 mm on an edge and an average thickness of 4.00 ± 0.02 mm. The chemical composition is given in Table 1. The glass samples were equally divided into two

groups. One group experienced a combined chemical tempering subsequent to thermal tempering process, hybrid tempering, and the other group was only strengthened by chemical tempering. The former group was firstly thermally tempered by force convective cooling in air at a pressure of 1.2 kPa after a heat soaking at 700 °C for 400 s to produce a residual compressive stress on the glass surface. After the thermal tempering process, all the two group of samples were chemically tempered simultaneously in an electric furnace at 420 °C for different time (3, 5, 7, and 14 h). The molten salt used was pure KNO₃ (purity > 99.9%). The glass surfaces were carefully cleaned with deionized water at the end of each procedure.

Table 1 Mean chemical composition of the glass used

Oxides	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	K ₂ O	CaO	Fe ₂ O ₃	Others
wt %	63.5	5.8	10.8	13.2	5.9	0.3	0.1	0.4

2.2 Compressive stress measurements

The compressive stress (CS) and depth of stress layer (DOL) of the specimens after chemical tempering were measured by birefringence stress measurement (FSM-6000LE, ORIHARA, Japan). The systematic errors for the CS and DOL are ± 20 MPa and ± 2 μ m, respectively. Each glass sample was measured at three random positions on the air and tin sides separately and the average CS and DOL values and error bar were obtained in order to confirm the reproducibility of the results.

2.3 FTIR spectroscopy measurements

Infrared reflection spectra was obtained using a Spectrum GX FTIR system (PerkinElmer) at the range 4000–400 cm⁻¹ with a specular reflectance accessory at room temperature to evaluate the surface structure difference between chemically

tempered and hybrid tempered specimens. The incident angle was 45° . Each spectrum was taken as an average of 16 scans collected over the frequency range of 1300–400 cm^{-1} with a resolution of 4 cm^{-1} . Three samples of each strengthening condition were analyzed in order to confirm the reproducibility of the results. A silver mirror was used as a standard reference for all measurements. All the results were rectified with Kramers-Kronig (K-K) relationship [24].

2.4 K^+ ion concentration depth profile measurements

The concentration depth profiles of the glass samples were measured by electron microprobe analysis (JXA-8100, JEOL, Japan). Beam conditions for all experiments were 44 nA current and 10 kV accelerating voltage. The glass specimens were firstly cut into two parts and embedded in a resin. Then the specimens were grinded and polished to get a flat surface. The fracture surface of glass was coated with thin carbon film by sputtering. The K^+ ion concentration was measured every 3 μm starting from the surface along the thickness direction. All the analyses were performed for each glass sample on the air and tin sides separately to investigate the different diffusion performance between the two sides in chemical tempering and hybrid tempering process. Calibration of the X-ray spectrum to ion concentrations was performed with glassy geological standards. All known ionic components were measured simultaneously to verify that K^+ and Na^+ were the only mobile species. Scans were performed three times at different locations on the cleaved surface.

2.5 Flexural strength measurements

Samples strengthened under different conditions were subjected to ring-on-ring

(ROR) biaxial flexural tests. The modulus of rupture (MOR) was determined using an Instron universal testing machine and a biaxial flexure test fixture as illustrated in our previous work [25]. The tin side can be distinguished by fluorescence obtained on irradiating with an ultraviolet lamp. In all cases, the air side was always used for the tensile side for better comparison. All specimens were taped on the tin side before test to retain fragments. Twenty specimens were tested for each condition using a displacement-controlled method with a cross head speed of 0.8 mm/min. The load at failure was used to calculate the strength of the specimen. Subsequently, the strength distributions were analyzed using a Weibull approach [26]. The random errors for Weibull modulus are obtained according to ASTM 1239-13 [27].

3 Results and discussions

3.1 CS and DOL results and interpretation

The CS and DOL of the chemically tempered specimens (referred to as CT in the figures) and thermally plus chemically tempered, also known as hybrid tempered specimens (referred to as TT+CT in the figures) on the air and tin sides are shown in Fig. 1. The CS decreases and the DOL increases with exchange time. With the exchange time prolonged, the amount of K^+ ions diffusing into the glass surface increases continuously which results in the increasing of DOL. However, increasing the exchange time may also lead to stronger stress relaxation [25, 28, 29]. Hence the CS decreases with exchange time.

It can also be seen from Fig. 1 that the hybrid tempered specimens show a lower CS and higher DOL values than the chemically tempered specimens. After thermal

tempering process, the fictive temperature of the glass specimens increases due to quenching from over the glass transition temperature by forced convection, using impinging air jet. This leads to a lower density on the glass surface [30]. Therefore, the diffusion of alkali ions into the glass matrix in thermally tempered glass becomes easier [31]. As a result, the hybrid tempered specimens show a higher DOL value. Meanwhile, the glass with an increased fictive temperature is more susceptible to stress relaxation, hence the hybrid tempered specimens show a lower CS value (Fig 1a). As can be noticed in Fig1a, the tin side always shows larger CS and lower DOL values whether the glass samples experienced a thermal tempering process or not, which is in accordance with our previous results [4, 22].

FIG1.TIF The CS and DOL as a function of exchange time (a) CS (b) DOL

3.2 FTIR spectroscopy measurements and interpretation

The FTIR reflectance spectra of the chemically tempered specimens and hybrid tempered specimens on the air and tin sides are shown in Fig. 2. The main peaks of IR results are observed at 1037 and 463 cm^{-1} and the two peaks are divided into two separate parts to provide more details. The insets in Fig. 2 are enlargements of the

peaks. The reflectance of different glass samples at 1037 and 463 cm^{-1} varies with exchange time. The reflectance on one side of the glass samples will be influenced by the other side because of the transparency of the glass, and total prevention of influence is quite difficult. However, the intensity of the reflected beam from the exposed surface is much stronger than that from the other side of the sample. Consequently, the reflected light is mainly composed of light from the exposed surface [32]. In addition, all results are rectified with K-K relationship [24] to avoid interference as much as possible.

Fig. 3 shows the percentages of reflectance at 1037 and 463 cm^{-1} for the two kinds of specimens as a function of exchange time. The percentages of reflectance of the two peaks decrease continuously with exchange time. The results also reveal that the chemically tempered samples show higher percentages of reflectance than the hybrid tempered samples.

The peaks at 1037 and 463 cm^{-1} in IR spectra are attributed to the Si-O stretching and Si-O-Si bending mode, respectively [32-34]. With the migration of K^+ ions into the glass, the total alkali concentration at the surface increases which lead to the destroy of bridging oxygens and the decrease of intensity of the two peaks [35]. The chemically tempered samples show higher percentages of reflectance than the hybrid tempered samples which indicates that the intensity of bridging oxygens in hybrid tempered glass is lower.

FIG2.TIF Infrared reflectance spectra (a) air side, 1037 cm^{-1} ; (b) air side, 463 cm^{-1} ; (c) tin side, 1037 cm^{-1} ; (d) tin side, 463 cm^{-1} .

FIG3.TIF Reflectance of different peaks as a function of exchange time: (a) 1037 and (b) 463 cm^{-1} . The solid and dash lines are guide to eyes.

3.3 Flexural strength results and discussions

Figure 4 shows the typical load-deflection relationships for glass samples with different exchange time at 420 °C. The fracture load varies with exchange time for both chemically tempered and hybrid tempered samples. The load-deflection curves become nonlinear with increasing load. The linear bending of glass in ROR fixtures is formulated in ASTM standards [36, 37]. However, these standards restrict the deflection to one quarter of the glass thickness. In our test results, the deflection of all samples exceed this restriction. Thus, the large-deflection theory should be considered when analyzing the flexural strength. A finite element analysis (FEA) method is used to solve the large deflection problem and the detailed method is described in our previous work [25].

FIG4.TIF Typical load-deflection relationships for glass samples with different exchange time at 420 °C.

According to the large-deflection theory [25], the modulus of rupture (MOR) of samples in different conditions are obtained. To analyze the flexural strength of the

glasses, the cumulative fracture probability (F) is calculated according to Eq. (1) [38-40]:

$$\{(\sigma_i, F_i)\} = \{(\sigma_i, (i - 0.5) / N)\} \quad (1)$$

in which N is the total number of the samples and i is the sample rank in ascending order of failure stress.

The Weibull modulus of these glasses are calculated according to Eq. 2:

$$F(x) = 1 - \exp(-V((\sigma - \sigma_u) / \sigma_0)^m) \quad (2)$$

Eq. 2 can be transformed into the usual double logarithmic form of the Weibull expression:

$$\ln \ln [1 / (1 - F)] = \ln V + m \ln (\sigma - \sigma_u) - m \ln \sigma_0 \quad (3)$$

where σ_0 is a scaling parameter, referred as a characteristic strength defined as the stress at which the F equals 63.2%. m is the Weibull modulus. V is the normalized volume of the samples. σ_u referred as the stress at which there is zero probability of failure. When it is taken to be zero, the Weibull distribution becomes a two-parameter model and the Weibull modulus can be obtained from the slope of the best straight fitting line of $\ln \ln [1 / (1 - F)]$ as a function of $\ln \sigma$ [26]. However, the use of the two-parameter Weibull approach can lead to overestimation of m and a high m value does not necessarily mean higher reliability [41, 42]. In addition, there's always a significant deviation from the straight fitting line at low values of $\ln \sigma$ when the two-parameter model is adopted. It implies that the assumption that the threshold σ_u is zero is no longer appropriate. Thus, the three-parameter Weibull distribution is adopted for fitting to get more accurate estimations of m . By using maximum

likelihood method, the m for the three-parameter Weibull distribution can be estimated.

In addition, the parameter estimate of the Weibull modulus (m) generally exhibits statistical bias which depends on the number of test specimens. To avoid the influence of sample amount and increase the accuracy of the m values, an unbiasing factor should be multiplied with m to obtain an unbiased estimate of m . According to ASTM 1239-13 [27], the unbiasing factor is 0.931 when the specimen number equals 20. Therefore, the m values are results of the Weibull modulus estimated from three-parameter Weibull model multiplied with 0.931. The upper and lower bounds of m are also calculated according to ASTM 1239-13. The upper and lower bounds on the Maximum Likelihood Estimate of the Weibull modulus (90% confidence interval) are obtained by dividing m by the relative normalizing factor, respectively. When the number of test specimens is 20, the normalizing factors are 0.791 and 1.449 for upper and lower bounds, respectively.

Figure 5 (a, b) shows the cumulative fracture probability (F) as a function of MOR and the Weibull modulus (m) results separately for raw glass and chemically tempered glasses. The same parameters of thermally tempered and hybrid tempered specimens are shown in Fig. 5 (c, d). The MOR at $\sigma_0=0$ ($F= 63.2\%$) and the normalized Weibull modulus (m) are listed in Table 2. It can be seen that the raw glass shows the lowest MOR (154 MPa) and m (1.01) value. Thermal tempering can slightly increase the MOR (192 MPa) and m (1.26) of glass. Nevertheless, the MOR and m of thermally tempered specimens are obviously lower than the chemically tempered and

hybrid tempered specimens. The MOR of chemically tempered glass for 12 h is largest at $\sigma_0=0$ ($F= 63.2\%$) while the MOR of hybrid tempered glass for 3 h is largest. Chemically tempered glass for 5 h shows the largest Weibull modulus ($m=3.61$) while the hybrid tempered glass for 3 h shows the largest Weibull modulus ($m=6.22$).

FIG5.TIF Cumulative fracture probability (F) as a function of MOR and

three-parameter Weibull plots for chemically tempered glasses (a, b) and hybrid

tempered glasses (c, d). The dash lines are the three-parameter Weibull fitting results.

Table 2. The MOR at $\sigma_0=0$ ($F= 63.2\%$) and the normalized Weibull modulus (m) of chemically tempered and hybrid tempered specimens for different exchange time (90% confidence interval).

Ion-exchange	CT		TT+CT	
Time (h)	MOR (MPa)	m	MOR (MPa)	m
0	154	1.01(0.75~1.37)	192	1.26(1.93~1.71)
3	504	1.87(1.39~2.54)	516	6.22(4.61~8.03)
5	518	3.61(2.68~4.91)	495	3.74(2.77~5.08)
7	519	1.84(1.37~2.50)	477	2.53(1.88~3.44)
12	528	2.07(1.53~2.81)	-	-
14	500	1.66(1.23~2.25)	447	1.42(1.06~1.93)

3.4 The diffusion coefficient results and interpretation

While there are two mobile species counter-diffusing in the chemical tempering process, charge neutrality requires that the diffusion rate be limited by the slowest species, believed to be the larger, heavier K^+ ion [43]. Thus the diffusion coefficients are all calculated from the K^+ ion concentration results.

Fig. 6 shows the K^+ ion concentration profiles on the air and tin sides of chemically tempered glasses at 420 °C for different exchange time. The K^+ ion concentration decreases with depth continuously and the K^+ ion concentration on the air side is always larger than that on the tin side which is in accordance with the DOL results. It can be seen that the tin-side curve is closed to the air-side one for the chemically tempered glass for 5 h (Fig. 6 c) which is different from the others. This phenomenon may be attributed to the combination effect of stress relaxation and structural relaxation. The diffusion rate of K^+ ions decrease with stress relaxation [44] and increase with structural relaxation [45]. The interaction of these two factors, coupled with the different compressive stress gradient on the two sides, may lead to

the result that the K^+ ion concentration profiles of the two sides closed to each other and this phenomenon may need further exploration in the future.

FIG.6. TIF K^+ ion concentration profiles on the air and tin sides of raw (a) and chemically tempered glasses at 420°C for (b) 3, (c) 5, (d) 7, (e) 12 and (f) 14 h

Boltzmann-Matano approach is employed to calculate the diffusion coefficient. Using concentration profiles of the exchanged ions, the diffusion coefficient as a function of ion concentration can be calculated by [46]:

$$D(c) = -\frac{1}{2t} \frac{dx}{dc} \int_0^c xdc \quad (4)$$

where $D(c)$ is the diffusion coefficient, c is the concentration of the migrating ion, x is the distance from the glass surface and t is the time of the diffusion process (in seconds). According to the experimentally obtained K^+ ion concentration profiles (Fig. 6), the concentration c can be expressed as a function of the distance x by a polynomial fitting line. Once the function is obtained, the diffusion coefficient can be calculated by Eq. (4).

Fig. 7 shows the potassium inter-diffusion coefficient of chemically tempered specimens as a function of K^+ ion concentration at 420 °C for different exchange time. The diffusion coefficient increases very slightly with the K^+ ion concentration, thus it can be assumed that the diffusion coefficient is independent of the K^+ ion concentration [4, 47].

FIG7.TIF Potassium inter-diffusion coefficient of chemically tempered specimens as a function of the K^+ concentration at 420 °C for different time: (a) air side, and (b) tin side. The dash lines are the linear fitting results.

Fig. 8 shows the K^+ ion concentration profiles on the air and tin sides of hybrid tempered specimens at 420 °C for different exchange time. The changing trend of the K^+ ion concentration is similar to the results of the chemically tempered glasses. The diffusion coefficients as a function of the K^+ ion concentration for the air and tin sides of hybrid tempered specimens are shown in Fig. 9. The slopes of the fitting lines in Fig. 9 are very small which indicates that the diffusion coefficient is almost invariant with the increasing of K^+ ion concentration. Hence, the assumption that the diffusion coefficient is independent with concentration is made and the average diffusion coefficient values through the whole K^+ ion concentration profiles are calculated and listed in table 3. This assumption is in accordance with previous work [10, 48]. The average diffusion coefficients (D) of chemically tempered and hybrid tempered specimens are calculated and shown in Table 3. The measured diffusion coefficients are in the range 10^{-14} - 10^{-15} m²/s which agree with previous measurements of K^+ - Na^+ diffusion coefficients in aluminosilicate glasses [4, 10, 11, 43, 49]. It can be seen the air side of the two kinds of glass samples show higher value of diffusion coefficients than the tin side which can be attributed to the hindered diffusion of K^+ ions by the tin in the glass [35]. The D values of chemically tempered samples decrease until the time up to 12 hrs, then it is increased when the time is 14 hrs. The diffusion coefficient decreases at first and then increases with time which is similar to the

results in the literature [50] and this phenomenon may be attributed to the combined effect of stress relaxation and structural relaxation. The diffusion coefficient is higher when stress is present [44] which leads to the decrease of diffusion coefficient with stress relaxation caused by the prolonged time. Glass with higher fictive temperature shows lower diffusion coefficient [45] which indicates the diffusion coefficient would increase with the lowering of the fictive temperature by structural relaxation. Therefore, the diffusion coefficient may be affected first by the stress relaxation which causes its decrease and then by the structural relaxation which causes its increase. For the hybrid tempered glasses, the thermal tempering process would lead to a lower density on the glass surface [30] which cause a stronger structural relaxation. The diffusion coefficient of the hybrid tempered samples may be mainly affected by the structural relaxation process which causes the continuously increasing of D .

FIG₈.TIF K^+ ion concentration profiles on the air and tin sides of hybrid tempered glasses at 420°C for (a) 3, (b) 5, (c) 7 and (d) 14 h

FIG₉.TIF Potassium inter-diffusion coefficient of hybrid tempered glasses as a function of the K^+ concentration at 420 °C for different time: (a) air side, and (b) tin

side. The dash lines are the linear fitting results.

Table 3. Average K^+ diffusion coefficients of chemically tempered and hybrid tempered specimens (95% confidence interval)

Time (h)	D ($\times 10^{-3} \mu\text{m}^2/\text{s}$) of the chemically tempered glasses		D ($\times 10^{-3} \mu\text{m}^2/\text{s}$) of the hybrid tempered glasses	
	Air side	Tin side	Air side	Tin side
3	8.0	5.9	3.8	2.0
5	4.5	2.6	4.2	2.9
7	4.2	1.7	11.4	3.1
12	2.2	1.1	-	-
14	9.7	2.5	14.8	6.4

3.5 Correlation between diffusion coefficient and flexural strength

The relationships between MOR and Weibull modulus with K^+ diffusion coefficient are shown in Fig. 10. The diffusion coefficient datum in Fig. 10 (a, b) are from the air side while the datum in Fig. 10 (c, d) are from the tin side. It can be seen that the MOR of both types of glass specimens decrease with the diffusion coefficient of the air side (Fig. 10a) and the chemically tempered glass shows higher value of MOR than the hybrid tempered specimens when the diffusion coefficient is the same. However, the MOR shows little dependency upon the diffusion coefficient of the tin side (Fig. 10b). The effect of diffusion coefficient on MOR for hybrid tempered glass is more remarkable than the chemically tempered glass. There is no significant relationship between Weibull modulus with the diffusion coefficient as shown in Fig. 10 (b, d).

With the increase of K^+ ion diffusion coefficient, the amount of K^+ ions diffusing into the glass surface per unit time increases. The alkali ions can destroy the bridging

oxygens on the glass surface [35, 51, 52]. The concentration of K^+ ion that migrate into the glass is higher than that of Na^+ ions leaving it which will cause an unbalanced electronic charge in the glass [35]. The atmospheric oxygen migrates into the glass surface during ion exchange to rebalance the electric charge [11], thus decreasing the concentration of the bridging oxygen content as shown in FTIR spectroscopy results (Fig. 4b). The decreased bridging oxygen content may lead to the decrease of MOR. In addition, it is believed that some network relaxation process can occur even at temperatures well below T_g [7, 53]. As the ionic radius of potassium is higher, the potassium ions prefer a higher oxygen coordination sphere compared to that of sodium. During K^+ - Na^+ ion exchange, there would be a two-stage local structure relaxation process since the coordination sphere difference which includes an initial fast relaxation involves rearrangement of the local potassium environment toward a mixed alkali glass and a slower relaxation toward the as-melted potassium end member [54]. The structure rearrangements may not be fully done when the K^+ ion diffusion coefficient is large. This may lead to more non-bridging oxygens and result in a lower flexural strength. In contrast, the MOR results show little dependency upon the diffusion coefficient of the tin side which may ascribed to the air side is always the tensile side in our ROR tests. In addition, the presence of significant larger flaws on the tin side of the glass samples due to contact damage by the rollers during the float glass process can lead to a significant different diffusion and mechanical behavior of the two sides [55, 56].

The surface compressive stress on the hybrid tempered specimens are lower than that of the chemically tempered specimens as shown in Fig. 2 which may lead to a lower flexural strength of the hybrid tempered glass. Moreover, the less bridging oxygens on the hybrid tempered glass surface than that of the chemically tempered specimens as shown in Fig. 4 may also lead to a lower flexure strength. After thermal tempering, a more disrupted structure is formed in the surface layers due to quick quenching from over the glass transition temperature which leads to a lower density and bending strength [30, 57]. Hence the diffusion of alkali ions into the glass matrix in thermally tempered glass is easier which may result in the effect of diffusion coefficient on MOR for hybrid tempered glass is more remarkable.

There's no significant relationship between the Weibull modulus with the diffusion coefficient which indicates that the variation of Weibull modulus is more complicated and the Weibull modulus is not only related to the diffusion process but also correlate with the surface conditions of the glass samples [25, 58] and other factors which needs further investigation.

FIG10.TIF The relationship between (a) MOR and (b) Weibull modulus with diffusion coefficient of the air side ($\times 10^{-3}$) and (c) MOR and (d) Weibull modulus with diffusion coefficient of the tin side ($\times 10^{-3}$). The solid lines are guide to eyes.

4 Conclusions

The correlation between $\text{K}^+\text{-Na}^+$ diffusion coefficient and mechanical properties of chemically tempered and hybrid tempered aluminosilicate glass are investigated. The air side of the two kinds of glass samples show higher value of diffusion coefficient than the tin side. The flexural strength of both types of glass samples decrease with the diffusion coefficient of the air side. The chemically tempered glass shows higher value of flexural strength than the hybrid tempered glass when the diffusion coefficient is the same. The effect of diffusion coefficient on MOR for

hybrid tempered glass is more remarkable than the chemically tempered glass. However, there's no significant relationship between Weibull modulus and the diffusion coefficient which implies that the influence factors for Weibull modulus are more complicated. The results would be useful in designing the strength of glass and guiding the strengthening process by chemical or hybrid tempering.

Acknowledgements

The authors thank Q. Zhou (Tsinghua university) for the technical support and useful discussions.

Fundings

This work is supported by The National Natural Science Foundation of China (Grant No. 51402273).

References

- [1] R. Gy, Ion exchange for glass strengthening, *Mater. Sci. Eng. B*, 149 (2008) 159-165.
- [2] A.K. Varshneya, Chemical Strengthening of Glass: Lessons Learned and Yet To Be Learned, *Int. J. Appl. Glass. Sci.*, 1 (2010) 131-142.
- [3] S. Kistler, Stresses in glass produced by nonuniform exchange of monovalent ions, *J. Am. Ceram. Soc.*, 45 (1962) 59-68.
- [4] L. Jiang, X. Guo, X. Li, L. Li, G. Zhang, Y. Yan, Different K^+Na^+ inter-diffusion kinetics between the air side and tin side of an ion-exchanged float aluminosilicate glass, *Appl. Surf. Sci.*, 265 (2013) 889-894.
- [5] X. Wu, R.E. Youngman, R. Dieckmann, Sodium tracer diffusion and ^{11}B NMR study of glasses of the type $(Na_2O)_{0.17} (B_2O_3)_x (SiO_2)_{0.83-x}$, *J. Non-cryst. Solids.*, 378 (2013) 168-176.
- [6] M. Potuzak, M.M. Smedskjaer, Alkali diffusivity in alkaline earth sodium boroaluminosilicate glasses, *Solid State Ion.*, 263 (2014) 95-98.
- [7] A. Varshneya, Kinetics of ion exchange in glasses, *J. Non-cryst. Solids.*, 19 (1975) 355-365.
- [8] F.O. Orgaz, J.F. Navarro, Kinetics of ion exchange and interdiffusion mechanisms in silico-aluminate glasses, *J. Non-cryst. Solids.*, 38 (1980) 605-610.
- [9] J. Torres-Castañón, A. Gorokhovskii, V. Zhabrev, A. Fuentes, J. Escalante-Garcia, E. German, Kinetics and Mechanism of the Interaction of Alkali Calcium Silicate Glasses with Salt Melts in the $KNO_3-Pb(NO_3)_2$ System, *Glass Phys. Chem.*, 30 (2004) 167-172.

- [10] J. Shen, D. Green, C. Pantano, Control of concentration profiles in two step ion exchanged glasses, *Phys. Chem. Glasses*, 44 (2003) 284-292.
- [11] B. Saggiaro, E. Ziemath, Diffusion coefficient of K^+ in ion exchanged glasses calculated from the refractive index and the Vickers hardness profiles, *J. Non-cryst. Solids.*, 352 (2006) 3567-3571.
- [12] G. Frischat, Simple method for the determination of ion-exchange profiles in glasses by micro-indentation tests, *J. Non-cryst. Solids.*, 3 (1970) 407-409.
- [13] D.J. Green, R. Tandon, V.M. Sglavo, Crack Arrest and Multiple Cracking in Glass Through the Use of Designed Residual Stress Profiles, *Science*, 283 (1999) págs. 1295-1297.
- [14] Vincenzo M. Sglavo, L. Larentis, D.J. Green., Flaw-Insensitive Ion-Exchanged Glass: I, Theoretical Aspects, *J. Am. Ceram. Soc.*, 84 (2001) 1827-1831.
- [15] Vincenzo M. Sglavo, David J. Green, Flaw-Insensitive Ion-Exchanged Glass: II, Production and Mechanical Performance, *J. Am. Ceram. Soc.*, 84 (2001) 1832-1838.
- [16] K. Anusavice, C. Shen, B. Vermost, B. Chow, Strengthening of porcelain by ion exchange subsequent to thermal tempering, *Dent. Mater.*, 8 (1992) 149-152.
- [17] H. Yoshimura, S. Guedes, C. Fredecicci, Glass dielectric with high mechanical and thermomechanical reliability produced by two-step tempering (thermal tempering+ ion exchange), *Matéria (Rio de Janeiro)*, 14 (2009) 845-860.
- [18] L.A. Pilkington, US Patent 2,911,759. , in: P.B. Limited (Ed.), 1959.
- [19] L.A. Pilkington, US Patent 3,222,154., in: P.B. Limited (Ed.), 1965.
- [20] L.A.B. Pilkington, Review Lecture: The Float Glass Process, *Proceedings of the*

Royal Society of London. Series A, Math. Phys. Sciences, 314 (1969) 1-25.

[21] O. Goodman, B. Derby, The mechanical properties of float glass surfaces measured by nanoindentation and acoustic microscopy, *Acta Mater.*, 59 (2011) 1790-1799.

[22] X. Li, L. Jiang, X. Zhang, Y. Yan, Influence of residual compressive stress on nanoindentation response of ion-exchanged aluminosilicate float glass on air and tin sides, *J. Non-cryst. Solids.*, 385 (2014) 1-8.

[23] J.A. Gonzalez Rodriguez, R.J. Hand, Evolution of the modulus and hardness of the tin and air sides of float glass as a function of hydration time, *Eur J Glass Sci*, 54 (2013) 36-41.

[24] X. Li, L. Jiang, L. Li, Y. Yan, Effects of HF etching on nanoindentation response of ion-exchanged aluminosilicate float glass on air and tin sides, *J Mater Sci*, 52 (2017) 4367-4377.

[25] L. Jiang, Y. Wang, I. Mohagheghian, X. Li, X. Guo, L. Li, J.P. Dear, Y. Yan, Effect of residual stress on the fracture of chemically strengthened thin aluminosilicate glass, *J Mater Sci*, (2016) 1-11.

[26] W. Weibull, A statistical distribution function of wide applicability, presented to the American society of mechanical engineers, *J Appl Mech.*, 23 (1951) 981-997.

[27] ASTM 1239-13, Standard practice for reporting uniaxial strength data and estimating Weibull distribution parameters for advanced ceramics, in, ASTM international, West Conshohocken.

[28] A.K. Varshneya, The physics of chemical strengthening of glass: Room for a new

view, J. Non-cryst. Solids., 356 (2010) 2289-2294.

[29] J. Shen, D.J. Green, Prediction of stress profiles in ion exchanged glasses, J. Non-cryst. Solids., 344 (2004) 79-87.

[30] A. Koike, S. Akiba, T. Sakagami, K. Hayashi, S. Ito, Difference of cracking behavior due to Vickers indentation between physically and chemically tempered glasses, J. Non-cryst. Solids., 358 (2012) 3438-3444.

[31] T.T. Ito S, Effect of cooling rate on structure and mechanical behavior of glass by MD simulation, J. Non-cryst. Solids., 349 (2004) 173-179.

[32] S.-i. Amma, J. Luo, C.G. Pantano, S.H. Kim, Specular reflectance (SR) and attenuated total reflectance (ATR) infrared (IR) spectroscopy of transparent flat glass surfaces: A case study for soda lime float glass, J. Non-cryst. Solids., 428 (2015) 189-196.

[33] F. Ezz-Eldin, T. Abd-Elaziz, N. Elalaily, Effect of dilute HF solutions on chemical, optical, and mechanical properties of soda–lime–silica glass, J Mater Sci, 45 (2010) 5937-5949.

[34] F. Geotti-Bianchini, L.D. Riu, G. Gagliardi, M. Guglielmi, C.G. Pantano, F. Geotti-Bianchini, L.D. Riu, G. Gagliardi, New Interpretation of the IR Reflectance Spectra of SiO₂-rich Films on Soda-Lime Glass, Glastech. Ber-Glass., 64 (1991) 205-217.

[35] B. Saggioro, E. Ziemath, Changes of physical properties of glass surfaces exposed to KNO₃ vapors, J. Non-cryst. Solids., 352 (2006) 2783-2790.

[36] S.P. Timoshenko, S. Woinowsky-Krieger, Theory of plates and shells: Bending

moments in a simply supported rectangular plate with a concentrated load, 1959.

[37] ASTM C1499-09, Standard test method for monotonic equilibrium flexural strength of advanced ceramics at ambient temperature, ASTM International, West Conshohocken.

[38] J. Zhang, D. Estévez, Y.-Y. Zhao, L. Huo, C. Chang, X. Wang, R.-W. Li, Flexural Strength and Weibull Analysis of Bulk Metallic Glasses, *J Mater Sci Technol*, 32 (2016) 129-133.

[39] A. Khalili, K. Kromp, Statistical properties of Weibull estimators, *J Mater Sci*, 26 (1991) 6741-6752.

[40] K. Trustrum, A.D.S. Jayatilaka, On estimating the Weibull modulus for a brittle material, *J Mater Sci*, 14 (1979) 1080-1084.

[41] H.L. Gao, Y. Shen, J. Xu, Weibull analysis of fracture strength for Zr₅₅Ti₂Co₂₈Al₁₅ bulk metallic glass: Tension-compression asymmetry and porosity effect, *J Mater Res*, 26 (2011) 2087-2097.

[42] R.V. Curtis, A.S. Juszczuk, Analysis of strength data using two- and three-parameter Weibull models, *J Mater Sci*, 33 (1998) 1151-1157.

[43] D. Morris, S. Myers, R. Cook, Indentation crack initiation in ion-exchanged aluminosilicate glass, *J Mater Sci*, 39 (2004) 2399-2410.

[44] F. Larcht'e, J. Cahn, The effect of self-stress on diffusion in solids, *Acta Metall.*, 30 (1982) 1835-1845.

[45] G. Roberts, J. Roberts, An oxygen tracer investigation of diffusion of water in silica glass, *Phys Chem Glasses*, 7 (1966) 82.

- [46] J. Crank, The mathematics of diffusion, Oxford university press, 1979.
- [47] S. Karlsson, B. Jonson, P. Sundberg, C. Stålhandske, Surface analysis of float glass using surface ablation cell (SAC). Part 2. Determination of the diffusion characteristics of K^+ – Na^+ ion exchange, *Glass Technol.*, 51 (2010) 55-62.
- [48] S. Karlsson, Modification of Float Glass Surfaces by Ion Exchange, in, LNU, 2012.
- [49] M. Patschger, C. Rüssel, Sodium/potassium ion exchange of a soda–lime–silica float glass: mechanical strength, hardness, stress profile and thickness of the ion exchanged layer, *Glass Technol.*, 56 (2015) 163-170.
- [50] M. Tomozawa, K.M. Davis, Time dependent diffusion coefficient of water into silica glass at low temperatures, *Mater Sci Eng. A*, 272 (1999) 114-119.
- [51] R. Hill, An alternative view of the degradation of bioglass, *J Mater Sci Lett.*, 15 (1996) 1122-1125.
- [52] V.M. Sglavo, A. Quaranta, V. Allodi, G. Mariotto, Analysis of the surface structure of soda lime silicate glass after chemical strengthening in different KNO_3 salt baths, *J. Non-cryst. Solids.*, 401 (2014) 105-109.
- [53] H.M. Garfinkel, C.B. King, Ion Concentration and Stress in a Chemically Tempered Glass, *J. Am. Ceram. Soc.*, 53 (1970) 686-691.
- [54] A. Tandia, K.D. Vargheese, J.C. Mauro, A.K. Varshneya, Atomistic understanding of the network dilation anomaly in ion-exchanged glass, *J. Non-cryst. Solids.*, 358 (2012) 316-320.
- [55] M.H. Krohn, J.R. Hellmann, D.L. Shelleman, C.G. Pantano, G.E. Sakoske,

Biaxial Flexure Strength and Dynamic Fatigue of Soda–Lime–Silica Float Glass, J. Am. Ceram. Soc., 85 (2002) 2507-2514.

[56] K.M. Entwistle, The fracture stress of float glass, J Mater Sci, 28 (1993) 2007-2012.

[57] N.M. Pavlushkin, S.I. Silvestrovich, V.M. Firsov, V.D. Kazakov, Structural state of the strengthened surface of severely tempered glass, J Mater Sci, 4 (1969) 479-484.

[58] A.B. Kulp, Analysis of Strength Variation in Glass Due to Ion Exchange, in, Virginia Polytechnic Institute and State University, Virginia, 2012.