Development of High Strength Chemically Strengthened Glass

Kosuke Kawamoto, Takashi Murata, Shinkichi Miwa, Masahiko Ohji, Hiroki Yamazaki
Nippon Electric Glass Co., Ltd. Shiga, Japan

Abstract

Newly developed chemically strengthened glass, T2X-1, is demonstrated. T2X-1 has high strength and excellent ion-exchange properties. Fracture strength of T2X-1 is 20% higher than conventional Alumino-silicate glass (CX-01). T2X-1 has twice as fast ion-exchange speed and durable compressive stress against four times more Na^+ contamination in molten KNO_3 than conventional Alumino-silicate glass (CX-01).

Author Keywords

Chemically strengthened glass; Cover glass; High strength; Ion-exchange property.

1. Objective and Background

It is common for touch panel makers to use chemically strengthened glass as cover glass to protect touch panel displays. Chemical strengthening is a well known process to increase fracture strength of glass. During the chemical strengthening process, glass substrate (generally containing Na^+ ion) is immersed in KNO_3 molten salt, the Na^+ ion site in glass surface is replaced by the larger ionic radius of K^+ ion. The difference in ionic radius of K^+ and Na^+ generates compressive stress on glass surface (Figure 1, 2). Depth of compressive stress layer is abbreviated to 'DOL'. Compressive stress value is abbreviated to 'CS'.

It is important to form a deep DOL and a high CS to guarantee high fracture strength of glass, [1][2]. A 40μm and more DOL and a 700MPa and more CS are recently recommended for the chemically strengthened glass. However, it is not easy to form a deep DOL and high CS in mass production due to the following reasons. One is stress relaxation during ion-exchange. The deeper DOL generally requires longer ion-exchange time. The ion-exchange time could be shortened by higher ion-exchange temperature. However, the higher temperature accelerates the stress relaxation of glass, resulting in a decrease of CS of glass. The other is a decrease of CS by Na^+ ion contamination in KNO_3 molten salt bath. Na^+ ions are released from glass surface into the KNO_3 molten salt during the ion-exchange process in mass production. High contamination of Na^+ ion in KNO_3 molten salt prevents the formation of higher CS of the chemically strengthened glass.

T2X-1 is a newly developed glass for chemical strengthening to solve these issues. T2X-1 is characterized by forming deep DOL and high CS in mass production. In this work, the fracture strength and the excellent ion-exchange properties of T2X-1 is discussed.

2. Experiments

The fracture strength, the DOL and CS of T2X-1 were investigated experimentally and compared with conventional Alumino-silicate glass and soda-lime-silicate glass.

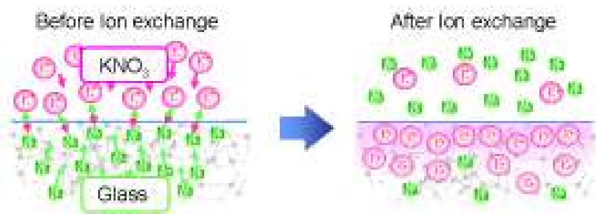

Figure 1. Schematic illustration of ion-exchange.

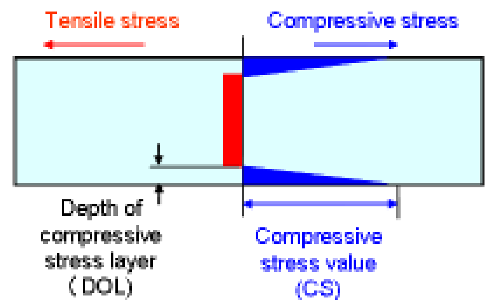

Figure 2. Schematic illustration of compressive stress layer.

Table 1. The Properties of T2X-1, CX-01 and SLS

Glass code	T2X-1	CX-01	SLS
Glass-system	Alumino-silicate	Alumino-silicate	Soda-lime-silicate
Density (g/cm^3)	2.45	2.54	2.5
Thermal Expansion Coefficient ($\times 10^{7}$°C) [30-380°C]	91	100	90
Young's Modulus (GPa)	71	75	71
Refractive Index (587.6nm)	1.50	1.52	1.52
Photo-Elastic Constant (nm/cm/MPa)	29.5	28.0	26.5
Dielectric Constant (1MHz)	7.7	7.7	-
Softening Point (°C)	860	760	730
Annealing Point (°C)	610	560	550
Strain Point (°C)	560	520	510

 ISSN 0097-966X/14/4503-1240-$1.00

Specimens: T2X-1, CX-01(conventional Alumino-silicate) and SLS (Soda-lime silicate glass) were prepared. T2X-1 and CX-01 are manufactured by the over flow down draw method, which is widely used for producing glass substrates for LCD. On the other hand, SLS is manufactured by the float process, which is also widely used for producing glass sheet for normal windows. Thickness of glass specimens are 0.7mm and properties of each glass are listed in table 1.

Ion-Exchange Properties: DOL and CS of the specimens treated under the same ion-exchange conditions were investigated. T2X-1, CX-01 and SLS, were ion-exchanged in KNO_3 molten salt (Na^+ ion concentration: 6000ppm) at 430°C for 4 hours. DOL and CS of the specimens were determined by using a surface stress meter FSM-6000 as shown in Table 2.

Three Point Bending Test: Specimens, T2X-1, CX-01 and SLS, of dimensions 135.4×85.2×0.7mm were prepared and individually ion-exchanged in KNO_3 molten salt. T2X-1, CX-01 and SLS were ion-exchanged in 430°C of KNO_3 molten salt for 4.5, 8 and 1 hours, respectively. Na^+ ion concentration in KNO_3 molten salt was 1,000ppm. DOL and CS were shown in Table 2.

A load tester was used for the three-point-bending test (Figure 3). Specimens are placed on stationary supports. The specimens were loaded at a rate of 3mm/min. The fracture strength in the 15th percentile, B15, was calculated. The results were treated by Weibull plot.

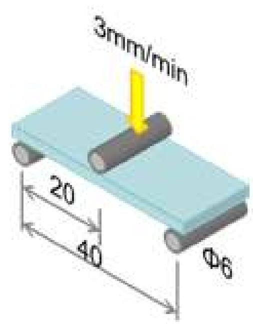

Figure 3. Schematic diagram of three-point-bending test.

3. Results

Ion-Exchange Properties: Figure 4 shows the DOL and CS of each specimen. The X axis shows CS and Y axis shows DOL. A plot on the upper right region of the graph indicates excellent ion-exchange properties.

It is clear that T2X-1 shows excellent ion exchange properties compared to conventional Alumino-silicate glass (CX-01). The deepest DOL and the highest CS have been formed under the same ion-exchange conditions. Only T2X-1 satisfies a 40μm and more DOL and a 700MPa and more CS in the ion-exchange condition.

Table 2. DOL and CS of T2X-1, CX-01 and SLS

Glass Code		T2X-1	CX-01	SLS
Ion-Exchange Properties (430°C-4h, Na:6000ppm)	DOL [μm]	46	33	23
	CS [MPa]	790	680	300
For Three Point Bending Test (430°C -4.5,8,1h, respectively, Na:1000ppm)	DOL [μm]	49	47	11
	CS [MPa]	860	740	550

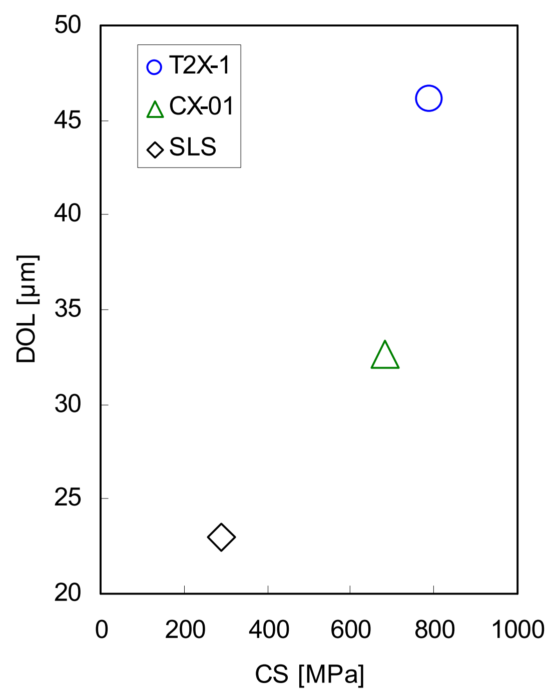

Figure 4. DOL and CS of T2X-1, CX-01 and SLS, ion exchanged in KNO_3 molten salt (Na^+ ion concentration: 6000ppm) at 430°C for 4 hours.

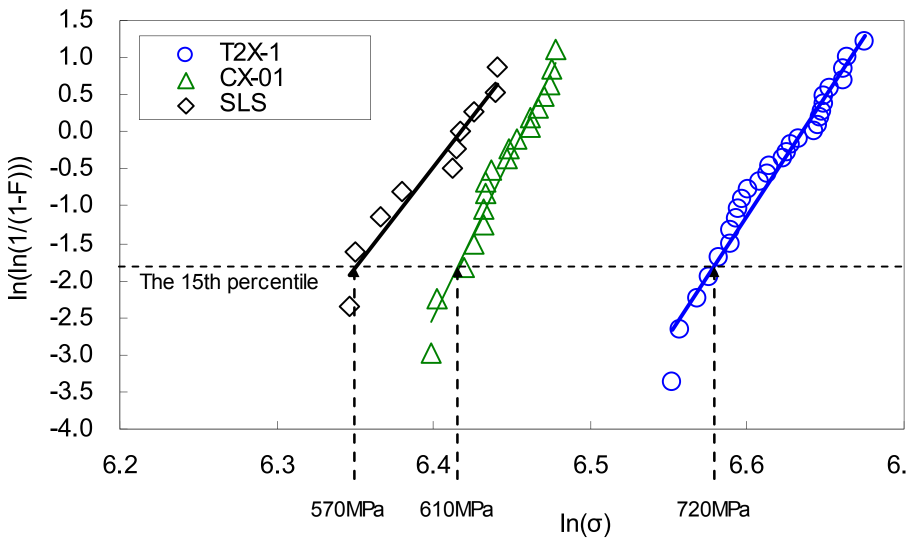

Figure 5. Weibull plot of T2X-1, CX-01 and SLS. σ[MPa] is fracture strength. F is failure probability calculated by Mean ranks.

Three Point Bending Test: Figure 5 shows a Weibull plot of fracture strength of T2X-1, CX-01 and SLS. The figure shows that the fracture strength of T2X-1 is clearly higher than that of CX-01 or SLS. B15 of T2X-1, CX-01 and SLS were 720MPa, 610MPa and 570MPa, respectively. B15 of T2X-1 was 1.2 times higher than that of conventional Alumino-silicate glass (CX-01).

4. Discussion

Ion-Exchange Properties (DOL): In this section, the benefits from the excellent ion-exchange properties of T2X-1 are discussed. Figure 6 shows DOL versus ion-exchange time of specimens, ion-exchanged in pure KNO_3 molten salt at 430°C for 1 to 8 hours. Remarkably, T2X-1 shows twice as fast ion-exchange speed than conventional Alumino-silicate glass (CX-01). T2X-1 achieves 40μm of DOL at 3 hours. On the other hand, 6 hours and over 8 hours are necessary for CX-01 and SLS, respectively. Ion-exchange time to exceed the same DOL can be shortened without any change in ion-exchange temperature by using T2X-1 instead of other glass materials. We believe that the shortened ion-exchange time of T2X-1 will increase productivity of ion-exchange process of chemically strengthened glass.

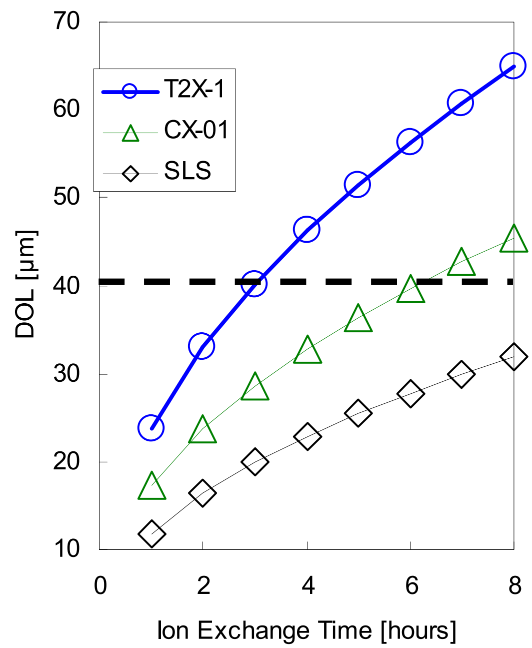

Figure 6. DOL of T2X-1, CX-01 and SLS versus ion exchange time.

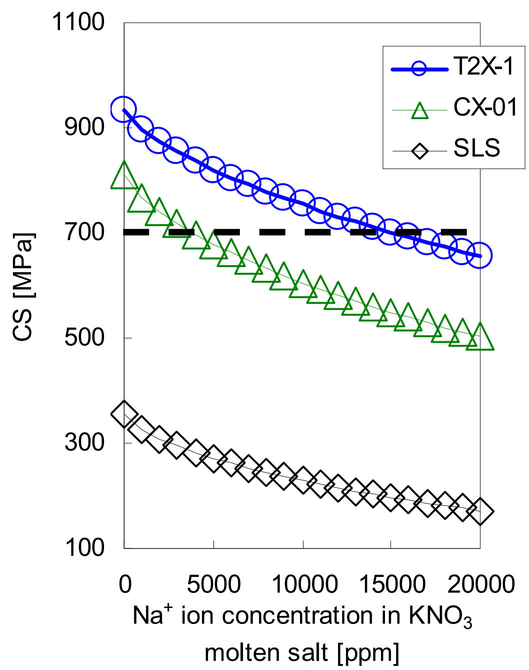

Figure 7. CS of T2X-1, CX-01 and SLS versus Na^+ ion concentration in KNO_3 molten salt.

Ion-Exchange Properties (CS): Figure 7 shows the CS of T2X-1, CX-01 and SLS treated under 430°C for 3, 6 and 13 hours, respectively, to create about 40μm of DOL versus various Na^+ ion concentrations in KNO_3 molten salt (0-20000ppm). CS of T2X-1, CX-01 and SLS were 930MPa, 810MPa and 360MPa, respectively when treated with pure KNO_3 molten salt. T2X-1 can keep high CS of over 700MPa until 15,000ppm, whereas, CS of CX-01 deteriorates to 700MPa at 4,000ppm. SLS cannot achieve 700MPa. By using T2X-1, higher CS can be obtained compared to using other glass materials even when ion-exchanged in highly Na^+ contaminated KNO_3 molten salt. In other words, CS of T2X-1 stays in a high standard of the recent recommendation even if the Na^+ contamination in KNO_3 molten salt is 4 times more than that of conventional Alumino-silicate glass (CX-01).

Fracture Strength: It is the most important for a cover glass to have high fracture strength in order to protect inner devices. This study showed that B15 of T2X-1 was 20% higher than that of conventional Alumino-silicate glass (CX-01). Therefore, the strength of cover glass could be increased by using T2X-1.

5. Conclusion

T2X-1 developed by Nippon Electric Glass has the following features.

- 20% higher fracture strength in the 15th percentile compared with conventional Alumino-silicate glass (CX-01).
- Twice as fast ion-exchange speed compared with conventional Alumino-silicate glass (CX-01).
- High and stable compressive stress which stays in a high standard of the recent recommendation even if the Na^+ contamination in KNO_3 molten salt is 4 times more than that of conventional Alumino-silicate glass (CX-01).

Therefore, T2X-1 has both enough strength for cover glass for touch panel devices and suitable ion-exchange properties for cover glass mass production. There is the possibility for touch panel makers to achieve both product quality improvement and cost reduction by using T2X-1.

6. References

[1] Sinue Gomez et al, “Designing Strong Glass for Mobile Devices”, SID 09 DIGEST, pp1045-1048

[2] James J. Price et al, “A Mechanics Framework for Ion-Exchanged Cover Glass with a Deep Compression Layer”, SID 09 DIGEST, pp1049-1051