

Characterization of Compressive Stress Layer of Chemically Tempered Glasses by the Ultrasonic Microspectroscopy Technology

超音波マイクロスペクトロスコピー技術による化学強化ガラスの表面応力層の評価

Mototaka Arakawa^{1†} and Jun-ichi Kushibiki²

(¹Grad. School Biomedical Eng., Tohoku Univ.; ² Grad. School Eng., Tohoku Univ.)
荒川元孝^{1†}, 櫛引淳一² (¹東北大院 医工, ²東北大院 工)

1. Introduction

Chemical tempering processes are conducted by immersing glasses containing Na⁺ ions into the molten salt containing K⁺ ions.¹⁾ Then, Na⁺ ions in the glasses are exchanged by K⁺ ions in the molten salt, and compressive stress layers are formed on the glass surfaces. Chemically tempered glasses with thicknesses of thinner than 1 mm were realized, and those are widely used as cover glasses of cell phones.

We proposed a method for evaluating chemically tempered glasses by the ultrasonic microspectroscopy (UMS) technology.^{2, 3)} We detected large changes of velocities of leaky surface acoustic waves and leaky surface skimming compressional waves caused by the chemically tempered processes by the line-focus-beam ultrasonic material characterization system.^{2, 3)}

In this paper, we characterize elastic properties of the surface compressive stress layer by measuring velocities and attenuation coefficients of longitudinal and shear waves and densities for non-tempered and tempered specimens of a chemically tempered glass.

2. Specimens

Two aluminosilicate glass substrates (Gorilla glass, Corning Inc.) were prepared for the specimens. One of them was immersed in the molten KNO₃. The other was not processed. The compressive stress and the depth of layer (DOL) were measured as 762 MPa and 49 μm, respectively, by a surface stress meter (FSM-6000LE, Orihara Industrial Co. Ltd.).

3. Method

Figure 1 shows a cross-section view of a chemically tempered glass having a thickness of h and a DOL of x . We extract elastic properties of

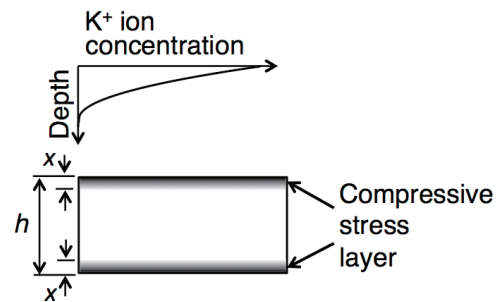


Fig. 1. Cross-section view and K⁺ ion concentration profile of chemically tempered glass.

surface compressive stress layer by assuming that the layer is homogeneous and isotropic. We also assume that the elastic properties in non-tempered region are same with those of the non-tempered specimen.

The density, velocity, and attenuation coefficients in the compressive stress layer are expressed as Eqs. (1)-(3).

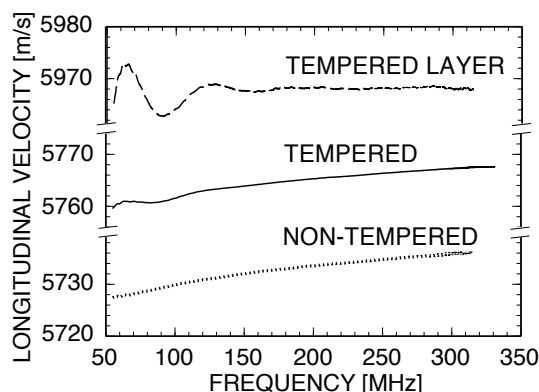
$$\rho_C = \rho_H \cdot [h/(2x)] + \rho_N \cdot [1 - h/(2x)] \quad (1)$$

$$V_C = \left[\frac{1}{V_H} \cdot \frac{h}{2x} + \frac{1}{V_N} \cdot \left(1 - \frac{h}{2x}\right) \right]^{-1} \quad (2)$$

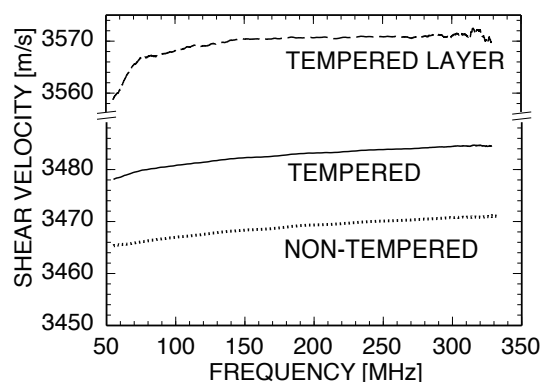
$$\alpha_C = \alpha_H \cdot [h/(2x)] + \alpha_N \cdot [1 - h/(2x)] \quad (3)$$

Here, ρ_C , V_C , and α_C are the density, velocity, and attenuation coefficient of the compressive stress layer, respectively. ρ_H , V_H , and α_H are those of the tempered specimen, and ρ_N , V_N , and α_N are those of the non-tempered specimen.

Velocities and attenuation coefficients of bulk waves of the specimens were measured by the complex-mode measurement method.⁴⁾ Density of the specimen was measured by the Archimedes method.



(a) Longitudinal velocity



(b) Shear velocity

Fig. 2. Frequency dependences of bulk-wave velocities for Gorilla[®] glass specimens.

4. Results and discussion

Measurement results of velocities for the non-tempered and tempered specimens are shown in Fig. 2. Longitudinal and shear velocities of the tempered specimen were larger than those of the non-tempered specimen. Figure 3 shows the measurement results of the attenuation coefficients. α_H were smaller than α_N for both longitudinal and shear waves. ρ_H and ρ_N were 2429.1 kg/m³ and 2433.0 kg/m³, respectively. ρ_H was 3.9 kg/m³ larger than ρ_N because of the exchange from Na⁺ ions to K⁺ ions.

ρ_C was obtained as 2460 kg/m³ by using Eq. (1) and the layer thickness of 49 μ m. Frequency dependences of V_C obtained by Eq. (2) were shown in Fig. 2. The density and velocities in the compressive stress layer were larger than those of the non-tempered and tempered specimens. The gradients of frequency dependences of V_C were smaller than those of V_H and V_N . α_C obtained by Eq. (3) were 0.4 dB/mm for longitudinal wave and 0.1 dB/mm for shear wave at 225 MHz, and α_C were smaller than α_H and α_N .

Pure SiO₂ glass takes three-dimensional random network structure composed of SiO₄ tetrahedra. The covalent bondings of Si-O-Si are

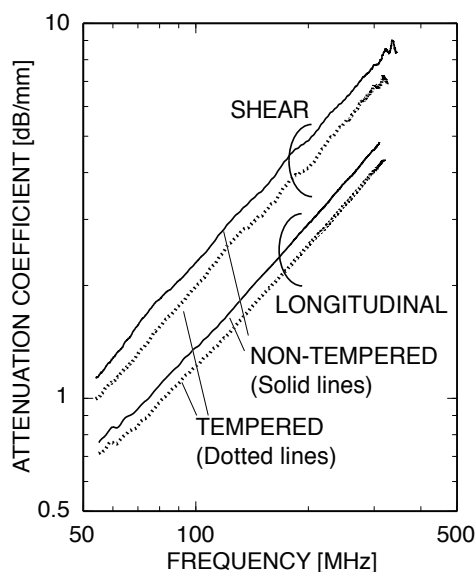


Fig. 3. Frequency dependences of attenuation coefficients of bulk waves for Gorilla[®] glass specimens.

partially broken by doping alkali metals and it causes formations of non-bridging oxygen. The alkali metals enter into interstices of the network. The interstices were reduced by exchanging Na⁺ ions into K⁺ ions, and then the elastic constants increased. As the concentration of dopants increase, gradients of velocity dispersion and attenuation coefficients of silicate glasses increased.⁵⁾ Therefore, stiffened structure of the compressive stress layer was detected from frequency dependences of velocities and attenuation coefficients of bulk waves.

5. Summary

In this paper, we clarified that the compressive stress layer of the chemically tempered glass was stiffened structure by measuring the bulk acoustic properties by the UMS technology.

Acknowledgment

This work was supported in part by KAKENHI Grant Number 26420380.

References

1. R. Gy: Mater. Sci. and Eng. **149** (2008) 159.
2. J. Kushibiki *et al.*: Proc. Symp. Ultrason. Electron. **34** (2013) 171.
3. M. Arakawa *et al.*: Proc. IEEE Ultrason. Symp. **46** (2006) 852.
4. J. Kushibiki, and M. Arakawa: J. Acoust. Soc. Am. **108** (2000) 1392.
5. J. Kushibiki *et al.*: IEICE Tech Rep. **107** (2007) 55.