Hydroxyl-concentration distribution near the binding interface formed by heating contacted flat silica glass surfaces at high temperature

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The hydroxyl-concentration distributions near the binding interface formed by heating contacted flat surfaces of various kinds of silica glasses at 1150°C were measured. The hydroxyl contents near the binding interface formed by the silica glass plates containing 1150 wt. ppm OH decreased, while those of the OH-free silica increased. As for a silica glass with ≈ 200 wt. ppm OH, the change in the hydroxyl content near the binding interface was within the variation of the hydroxyl content, ±≈ 20 wt. ppm.

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Vitreous silica has a low thermal expansion and high optical transmission over a wide wavelength region. By utilizing these properties, this material is used in optical applications. Some optical products, such as the cells used for spectroscopic measurements and fry-eye lenses used for homogenizing a laser beam, are fabricated by bonding pieces of silica glasses. The silica glasses can be bound by heating the contacted polished flat surfaces. Upon heat treatment, the structure of the silica glass changes.1) The structural change proceeds from the surface. One of the authors and colleagues studied the structural change in the cross section of a silica glass tube by heating with an oxy-hydrogen flame.2)–4) To understand the effect of the hydroxyl group on the binding of the silica glasses, we measured the OH-concentration distribution around the interface formed by binding of the silica glass surfaces in this study.

Three kinds of silica glasses, ES, NP and HPR, were used. These sample names are the trademark of the Tosoh Corporation. ES is directly produced by the flame hydrolysis of silicon tetrachloride in an oxy-hydrogen flame and contains ≈ 1150 wt. ppm OH. NP is produced by melting natural quartz powder in an oxy-hydrogen flame and contains ≈ 200 wt. ppm OH. HRP is produced by melting natural quartz powder in an electric furnace and contains less than 1 wt. ppm OH. These silica glasses cut into plates 10 × 30 × 3 mm with surface faces of 3 mm thick are optically polished. Two such plates are contacted in an electric furnace and heated under atmospheric conditions at 1150°C for 20, 60 or 90 min, then allowed to naturally cool to room temperature. We shall represent the sample formed by the binding of ES and HRP as ES + HRP, etc. The six combinations of the silica glass species between the same species (ES + ES, NP + NP, HRP + HRP) and different species (ES + NP, ES + HRP, NP + HRP) were measured. After the binding, the test piece with a 0.51 ± 0.1 mm thickness and polished surfaces were cut from the center of each combined glass. The infrared (IR) absorption spectra were measured by a Fourier-transform IR spectrophotometer (Jasco FT/IR–660 Plus) equipped with an IR microscope unit (a Jasco FT/IR–30). The IR beam was focused on the upside surface of the test piece. The aperture size of the measurement region was 30 × 100 μm. The longer side of the aperture was set parallel to the binding interface. The resolution of the wavenumber of the measurement is 4 cm–1 and 60 measurements were accumulated. The hydroxyl concentrations were determined by the peak intensity of the absorption peak at 3650 cm–1 with the molar extinction coefficient of 77.6 dm3 mol–1 cm–1 (Ref. 5).

Figure 1 shows the hydroxyl-concentration distribution of the entire intersection of the binding samples. Figure 2 shows the hydroxyl distribution near the binding interface. In sample ES + ES, the hydroxyl concentrations decreased near the surfaces and the binding interface. The change in the hydroxyl content of sample NP + NP could not be conclusively determined because the spatial dispersion of the hydroxyl content was ±≈ 20 wt. ppm. In the sample HRP + HRP, on the other hand, the hydroxyl content increased near the surfaces and the binding interface. In the piece of the silica glass with free surfaces, the hydroxyl content of a high-OH-containing silica glass, such as ES, decreases, and that of a low-OH-containing silica glass, such as HRP, increases near the surface upon heat treatment. Even in a hydrogen-rich atmosphere, such as in an oxy-hydrogen flame, the hydroxyl content near the surface of OH-rich sample, such as ES, decreases.2)–4) Although the mechanism of the change in the OH content upon heat treatment is unknown, this fact suggests the existence of a characteristic value of the hydroxyl content at which the hydroxyl content near the surface remains constant upon heat treatment. In NP, the trend in the change of the hydroxyl content near the surface depends on the heat-treatment condition. In ref. 4), the OH content near the surface of a sample with 200 wt. ppm OH slightly increased. However, when heat-treated in a humid atmosphere, the sign of the change in the OH content depended on the heat-treatment temperature and time.2) This fact suggests that the characteristic hydroxyl content could be dependent on the heat-treatment conditions and could be around 200 wt. ppm. The change in the OH content near the binding interface must be
due to the same mechanism that changes the OH content near the free surface. The source of the OH in HRP could be the adsorbed water on the binding interface or the water vapor in the atmosphere that diffuses through the binding interface. In the interface formed by the binding of the silica glass plates with different amounts of OH, ES + NP, ES + HRP and NP + HRP, the hydroxyl content smoothly changes near the binding interface.

Figure 2 shows the hydroxyl-concentration distribution near the binding interface. The concentration of the minimum value (at the interface) of ES decreases with the increase of heating time between 20 and 60 min. At the heating time of 90 min, on the other hand, the distribution around the interface becomes flat. As for NP, the OH content seems to increase at the binding surface, and the distribution becomes flat at the heating time of 90 min. Since the spatial dispersion of the OH content in NP is quite high, this change could not be true. The hydroxyl contents near the binding surface of the HPR increase. The distribution of the hydroxyl content is asymmetric around the binding interface. As the heat treatment time increases, the hydroxyl content becomes smaller compared to that at the heat treatment time of 20 min. This fact shows that the hydroxyl groups diffused during the heat treatment and tended to be uniform as in the case of the ES.

As for the binding of the different types of silica glass plates, the hydroxyl content smoothly changed around the binding inter-
face (Fig. 2). The heat-treatment-time dependence of the curve is hard to distinguish. Figure 3 shows the normalized hydroxyl-concentration distribution near the binding interface. The change in the hydroxyl content near the binding interface of NP + HRP is relatively steep compared to those of ES + NP and ES + HPR. The smooth change is not only due to the real distribution, but also the apparent one due to the focused beam of the measurement. That is, if the OH content stepwise changes at the binding interface, the measured hydroxyl contents smoothly changes. The solid curve in Fig. 3 is the calculated curve when the hydroxyl content stepwise changes; here we used the values of the numerical aperture (NA) of 0.45 for the microscope unit, the refractive index of 1.42 at 2700 nm evaluated by the formula proposed by Malitson,7) and the sample thickness of 0.51 mm. The change in the hydroxyl content based on the theoretical curve is similar to the observed ones. This fact suggests that the effect of the hydroxyl diffusion is hard to distinguish in the present measurements.

In summary, the hydroxyl content distributions around the binding interface that are formed by heating of the contacted flat polished surfaces of silica glasses were measured. The hydroxyl contents near the binding interface of a silica glass with a 1150 wt. ppm OH decreased, while those of the hydroxyl-free silica glass increased. Near the binding interface formed by the binding of the silica glass plates containing 200 wt. ppm of OH, the amount of the OH-content change is within the spatial variation of the hydroxyl content of the material. As the heat treatment times increased, the amount of changes near the interface decreased. This suggests that the hydroxyl groups near the interface diffuse and distribute uniformly in the glass. The hydroxyl distribution near the interface formed by binding different kinds of silica glasses smoothly changed. This could be quite apparent due to the observation geometry of the IR beam and it was hard to distinguish the effect of the hydroxyl group diffusion.

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References
6) Unpublished.