DIFFUSION OF WATER INTO SILICA GLASS

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Diffusion of water into silica glass influences the properties of glass. Most applications of silica glass are at relatively low temperatures. The water diffusion data, however, are insufficient in the low temperature region.

Anomalous behavior of water diffusion into silica glass occuring at low temperature has been reported. One result is that the Arrhenius type plot of the effective diffusion coefficients for water gives two lines with different slopes in the high and low temperature regions, with a gap between the lines at around 500°C. The other problem is that surface concentration of OH (solubility) and the effective diffusion coefficients depend on treatment time in the initial stage. The value of the surface OH concentration increases with increasing temperature at low temperatures, while at high temperature, the reverse occurs.

In order to make these unique features clear and to try to point toward a true diffusion mechanism, the following experiments have been carried out. The water diffusion was measured under different vapor pressures and in H_2O and D_2O vapor and with various types of silica glass. The OH concentrations in the glass were determined by the analysis of the IR absorption band at 3670 cm^{-1} using an FTIR spectrometer. Finally, water penetration profiles were obtained by successively etching away thin glass layers.

The features of diffusion profiles in the higher and lower temperature regions are dissimilar in behavior; the former has a convex upward diffusion profile, while the later nearly a concentration-independent curve. Some of the OH absorption bands in 3000-4000 cm^{-1} region shift to the lower wave number and a new band appears around 3400 cm^{-1} when the temperature decreases below 500°C and the vapor pressure increases. The effective diffusion coefficient increases with increasing vapor pressure. One explanation would be that the hydrogen bonded hydroxyl group is increasing under the conditions concerned. Also, most hydroxyls in glass are exchangeable with penetrating water. The above tendencies are similar for different types of silica glass, but the amount of uptake water is differs among them.

On the basis of the results, some models for diffusion and reaction of water with silica glass will be discussed.

Introduction

The solubility and diffusion of water into silica glass from the vapor phase depend on the thermal history of the glass, the SiOH content, the vapor pressure and temperature. The research by Roberts and co-workers in the 1960's clarified these mechanisms[1-6].

The necessity for further studying the diffusion of water in silica glass technology is as follows. First, in modern electronic technology an important process is to produce an insulating SiO_2 film oxidized by water on semiconductor silicon.[7] Also, as the presence of OH in silica glass changes the refractive index, the migration of OH species might form an unexpected index distribution.[8] Another reason is that the formation of SiOH due to water diffusion causes light attenuation in wave guides. Finally, the H_2 and H_2O gas release from silica glass influences the life of lamps with silica glass envelopes.[9]

In order to deal with the above problems, the essential nature of water diffusion in silica glass has to be understood over a wide temperature range, especially at lower temperatures. However, most diffusion data are limited to a temperature range of 600 - 1200°C and are missing at lower temperatures.[10]

In this review the diffusion at lower temperatures, which is important for practical use of silica glasses, will be examined compared with the results at high temperatures.

Differences water diffusion behavior between high and low temperature regions

These results, obtained from water diffusion experiments on a low-water-content silica glass Suprasil W over a wide temperature range, exhibit dissimilar diffusion behavior in the temperature regions above and below 500°C.[11] In this experiment, the heat-treatments were carried out under a constant water vapor pressure of 47 kPa and the OH contents in the glass samples were determined by the intensity of the IR absorption band at 3670 cm^{-1} using an FTIR.

The water uptake versus square root of heat-treatment time shows a linear relation at high temperatures as expected from diffusion with a constant surface concentration but at low temperatures a nonlinear relation occurs such as expected from diffusion models for a surface evaporation condition. According to the analysis of diffusion-time-dependent profiles of OH as shown in Figure 1 however, the surface concentration over the whole temperature region depends initially on diffusion time and increases with time to reach a steady state solubility value at a given temperature. The time to reach this solubility value is just 15 hours at 650°C under 47 kPa water vapor pressure, while at 350°C the surface concentration did not reach this value even after 450 hours.[12] The surface concentration, regarded as the solubility, for the longest treatment time at each temperature increases with decreasing in temperature at higher temperatures but at lower temperature the trend is just the opposite.

Another unique feature in the profiles is that the diffusion coefficient for short treatment times is larger than that for long times. For example, Figure 1 shows that the diffusion depth normalized by the square root of diffusion time is greater for a shorter diffusion time. Furthermore, the profiles at low temperatures are close to those expected for a constant diffusion coefficient, whereas with an increase in heat-treatment temperature, the profiles begin to show features of concentration-dependent diffusion. Models of the water diffusion mechanism have been suggested and argued on the basis of this dependence.

Effective diffusion coefficients, D_e were calculated from the profiles for a long heat-treatment time, t, at a given temperature, using the surface concentration, C_i, the total uptake, M, of water and the following relation,

$$D_e = (\pi/t)(M/2C_i)^2 \qquad\qquad (1).$$

An Arrhenius plot of D_e is shown in Figure 2. The dotted line has a break at 500°C and anomalous values appear at 450°C. It might be assumed that the profiles

at 450°C are the superposition of two profiles with different diffusion coefficients similar to Lanford et al. who found two diffusion coefficients for water diffusion into silica glass at 90°C, 6×10^{-18} and $10^{-15} cm^2/s$.[13]

The activation energy is about 40kJ/mol at the lower temperatures and 80kJ/mol at the higher ones.

Change of OH absorption peak shapes with heat-treatment conditions

Figure 3 shows typical IR absorption spectra containing the OH stretching band in silica glass specimens which were treated at different temperatures and vapor pressure. The different treatments give different peak shapes. The profile "a" due to a specimen heat-treated at 650°C coincides with those of water-containing silica glass as-recieved such as Type II silica glass, and this type of profile is seen in specimens heat-treated at temperatures higher than 550°C.

Below 550°C, the peak shifts to lower wavenumbers and the absorption band broadens and has a shoulder such as the profile "b" in Figure 3. It is believed that these phenomena are caused by an increase in hydrogen bond association.[14] In order to demonstrate the characteristic change of the bonds with temperature, the peak was separated into four components following Walrafen and Samanta's method.[15] The shifts in peak wave numbers of the four components with temperature are shown in Figure 4. The lower wavenumber components show larger shifts to the low wavenumber side with decreasing temperature. This onset of the peak signal change occurs in the same temperature range as the diffusion behavior change discussed above.

Water diffusion in various types of silica glass

The above results were obtained from a sample of Suprasil W. In order to examine whether or not the water diffusion behavior mentioned above is generally acceptable, water diffusion experiments have been carried using various types of silica glass listed in Table 1, which involve differences in starting materials,

preparations, water contents and other impurities. In order to make the behavior clear even in a glass with high water content, D_2O was used as a isotope tracer.[16]

The net uptake of water (H_2O and D_2O) at 350°C does not initially have a linear relationship versus square root of time and the vapor uptake quantities are widely different among the glasses as shown in Figure 5. Much more water is captured in synthesized silica glasses than in quartz glasses. The OH which exists in glass such as Type III can easily exchange sites with D_2O, and at the same time H_2O is removed from the glass.

Figure 6 shows diffusion profiles of OD in glasses treated in D_2O vapor at 350°C for 256 hours. The synthesized silica glasses have high surface concentrations of OD compared with quartz glasses. It is not clear from the results whether the differences appearing in various glasses are due to their nature or due to thermal history. The penetration depth was almost the same in all of the glasses examined. As the values of diffusion coefficients for D_2O are almost the same, the diffusion rate does not appear to be seriously affected by the initial OH content contrary to a previously published conclusion.[2]

One remarkable dissimilarity in these types of silica glass appears in IR absorption spectra after heat-treatment. The spectrum (profile "b") shown in Figure 3 is for Type IV silica glass(VAD-F) with a very low water content treated in 47 kPa water vapor at 350°C for 256 hours, and has a new peak at $2820cm^{-1}$. This peak only appears in Type IV glass with very low water contents such as VAD-F and Suprasil W. Since the peak position is near the $2762cm^{-1}$ (3.62 μm) peak of the OH absorption band due to hydrogen bonds associated with non-bridging oxygen[17] and these glasses contain many peroxy bridges, this new band might occur by the formation of hydrogen bonds associated with non-bridging oxygen in the presence of peroxy bridges. This peak does not appear in any glasses treated at temperatures higher than 550°C.

Water diffusion treatment in autoclave

The OH absorption band spectrum for a specimen treated in a autoclave at 250°C is shown by profile "c" in Figure 3, in which an intense and broad peak at 3400 cm^{-1} is involved and assigned to molecular water.[18] The existence of molecular water in glass will be assumed from this result. The absorption band at 2820cm^{-1} (profile "c" in Figure 3) is also present only in the ~~above~~ two glasses discussed above.

The two IR absorption intensities at 3670 and 3400 cm^{-1} both increase linearly with the square root of treatment time. The concentration profiles for OH and H$_2$O in silica glass, Suprasil W, are shown in Figure 7 and demonstrate higher OH surface concentration and larger penetration depth for OH and H$_2$O compared with that for treatment under a low vapor pressure, 47 kPa, also shown in the figure. Effective diffusion coefficients calculated from Eq. 1 are 4 to 6 times larger than those for the 47 kPa treatment.

In order to qualitatively examine the diffusion and reaction of water in glass, specimens were treated in a autoclave at 200°C for 240 hours, then suddenly transfered to a furnace kept at 650°C in air. The changes of peak intensities at 3670, 3400, and 2820 cm^{-1} are plotted versus heating time in Figure 9. The peak related to molecular water disappears quickly, while the OH peak at 3680cm^{-1} first abruptly increases and then gradually decreases, with further heating. The peak at 2820cm^{-1} decreases at a rate similar to the peak at 3670cm^{-1} and eventually disappears, because treatment at 650°C does not promote the formation of this peak. Molecular water which exists in glass at low temperature reacts with the silica network at higher temperature to produce more SiOH groups and then can escape from the surface as molecules.

Modelling diffusion of water into silica glass

Mechanisms for diffusion of water into silica glass have been modeled by

many researchers.[5,7,19,20]

Roberts and co-workers proposed a diffusion mechanism in which associated proton and hydroxyl groups jump from SiOH groups to Si-O-Si bridges on the basis of the results for a diffusion study using labeled water, $H_2^{18}O$.[5] Doremus objected to their model and proposed that water diffuses as molecules into silica glass, subsequently reacts with SiO_2 network, and then an equilibrium is set up between [H_2O] and [-SiOH].[7,19] A water penetration profile calculated from the model coincided with experimental data. This model is the most plausible at present but cannot explain the low temperature profiles. Taking this into account, Tomozawa suggested that both molecular water and hydroxyl water can diffuse and are in equilibrium.[20]

If the results for water diffusion over a wide temperature range are considered in modelling the diffusion mechanism, these models will need correction and revision.

Wiesenfeld et al. have modeled the mechanism of diffusion and reversible reactions of hydrogen at finite rates in silica glass.[21] The model is shown schematically in Figure 9 with a modification including water diffusion and reaction.[11,12] According to the model, water molecules initially diffuse intesticially into silica glass, and then some of the molecules react with the silica network to form immobile hydroxyl ions and the rest pass through the network or stay without reaction. The reaction with the network is reversible, having finite forward and reverse rates, k_f and k_r. It might be qualitatively argued that this time-dependent reaction causes the initial, anomalous diffusion of water into silica glass.

Summary

This review has dealt with water diffusion into silica glass at low temperatures. There are many differences between low and high temperatures in

diffusional behavior and in the state of the water. In the initial stage, the diffusion deviates from steady state conditions. At low temperatures, the activation energy for diffusion has a lower value and the degree of hydrogen-bonding association increases. When glass is heat-treated under high water vapor pressure, molecular water co-exists with hydroxyl one in the samples. In order to explain the results, a favorable model is discussed.

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Table 1

SAMPLE GLASSES

Classification	Preparation method	Raw material	H_2O in ppm
Type I	electrical melting in vacuo or inert gas	quartz	5 – 10
Type II	H_2+O_2 plasma	quartz	130 – 200
Type III	H_2+O_2 plasma	$SiCl_4$	900 – 1300
Type IV (Suprasil W)	HF plasma	$SiCl_4$	– 1
(VAD-F)	VAD treated with Cl_2	$SiCl_4$	– 0.05
(VAD-S)	VAD treated without Cl_2	$SiCl_4$	50 – 70

Fig. 1

(a)

(b)

Fig. 2

Moulson & Roberts
Burn & Roberts
Nogami & Tomozawa
Lanford et al.
Wakabayashi & Tomozawa

Fig. 3

c : 250°C,   4MPa

b : 350°C,
47kPa

a : 650°C,   47kPa

Absorbance (arbitary)

4000   3500   3000   2500

Wave number / cm^{-1}

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Plot of Absorption coeff. / cm^{-1} (y-axis, 0 to 30) versus X / μm (x-axis, 0 to 20) for Suprasil W, 200°C, 240 hr. Curves labeled OH (1.55 MPa), H$_2$O (1.55 MPa), and OH (47.3 kPa).

Fig. 8

Plot of Absorbance versus t / min for VAD-F. Curves shown: -SiOH ($3670\ cm^{-1}$), H_2O ($3400\ cm^{-1}$), and SiOH···O ($\times 10$) ($2820\ cm^{-1}$). Labels on the figure read "VAD-F", "Heat-treatment at 650 °C in air after autoclave treatment", and "As treated in autoclave at 200 °C, for 240 h".

Fig. 9

$$J_{H_2O} = -D_{H_2O} \frac{d[H_2O]}{dx}$$