Original Paper

Thermal dehydroxylation of porous glass

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The thermal removal of hydroxyl groups from porous glass tubing depends on both temperature and time. The general relationship between these two parameters and the residual hydroxyl content in 96 % SiO_2 (by weight) reconstructed glass was determined by subjecting porous glass tubes to various temperatures in vacuum and in dry air. The temperature for maximum removal of water decreases as the hold time increases. The optimum temperatures result from a balance in rates of water diffusion and glass sintering which retards diffusion. Increasing the total pressure of the atmosphere surrounding the porous glass during the degassing cycle decreases the net degassing rate. The role of other factors such as composition of the porous glass and pore structure are briefly mentioned.

Thermische Entwässerung eines porösen Glases

Die thermische Austreibung von Hydroxylgruppen aus porösen Glasröhren hängt von der Temperatur und Zeit ab. Die Beziehung zwischen diesen zwei Parametern und dem verbleibenden Hydroxylgehalt des aus 96 % SiO_2 bestehenden verdichteten Glases wurde durch Wärmebehandlung von porösen Glasröhren bei verschiedenen Temperaturen in Vakuum und im trockenen Luftstrom ermittelt. Die Temperatur für die maximale Austreibung von Wasser fällt mit Verlängerung der Haltezeit (Verweilzeit bei einer gegebenen Temperatur) ab. Die optimalen Temperaturen ergeben sich aus einem Gleichgewicht zwischen den Wasserdiffusions- und Schrumpfungsgeschwindigkeiten des porösen Glases, die die Diffusion verzögern. Die Erhöhung des Absolutdruckes der Atmosphäre, die das poröse Glas während der Entgasungsbehandlung umgibt, erniedrigt die Austreibungsgeschwindigkeit des Wassers (OH-Gruppen). Die Rolle anderer Parameter wie die chemische Zusammensetzung des porösen Glases und die Porenstruktur werden kurz erwähnt.

1. Introduction

The removal of water from porous glass prior to consolidation into a clear impervious glass is important since water in the glass structure not only lowers its annealing point [1] but also can lead to outgassing or even reboil on reheating [2].

This paper deals with the removal of hydroxyl groups in porous glass and the general relationships between time and temperature of heating and residual water content in the final glass. The role of other factors such as composition and pore structure of the porous glass are briefly mentioned.

2. Experimental part

2.1. Specimens

Porous glass [3], a high-silica body with continuous pore structure (≈ 5 nm), was used in this study in the form of 12 mm-diameter tubing with a 1.2 mm thickness.

The composition of the porous glass on the basis of its ignited weight (in wt %) is 96 % SiO_2, 3 % B_2O_3, 0.4 % $R_2O_3 + RO_2$ (chiefly Al_2O_3 and ZrO_2), and traces of Na_2O.

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2.2. Firing of specimens

The porous glass specimens which had been dried for 1 h in an electric oven at 110 °C were transferred into a 45 mm-diameter silica tube and a vitreous refractory mullite tube. The tubes, which were adjacent to one another, and their contents were heated to the desired hold temperature at a rate of 160 K/h. Those in the silica tube were heated in a stream of dry air (dew point = −79 °C), the others in vacuum (≈ 66.7 Pa) maintained by continuous pumping with a DUO-Seal Welch vacuum pump.

After reaching the desired temperature, the specimens were held for 1, 4 and 8 h, and then further heated at 160 K/h to 1230 °C (30 min hold) to consolidate the porous structure into a clear impervious glass.

2.3. Infrared measurements

Spectrographic measurements were made through one wall of the fired specimens with a recording infrared spectrometer (Model 221, Perkin-Elmer Corporation). The absorption coefficients β_{OH} were calculated using equation (1):

$$\beta_{OH} = \frac{1}{t} \log_{10} \frac{T_{2.6}}{T_{2.72}}, \qquad (1)$$

where t = sample thickness in mm, $T_{2.6}$ = transmittance in percent at 2.6 μm, and $T_{2.72}$ = transmittance at the peak of the OH band at 2.72 μm.

3. Results

The β_{OH} values of the final glasses are shown graphically as a function of temperature in figures 1a and b. The curves, which are based on data given in table 1, go through a minimum indicating that there is an optimum temperature for each hold for dehydroxylating porous glass. The minima for the vacuum-fired specimens are lower than those for the dry-air fired glasses, suggesting that degassing of the porous structure prior to pore closure proceeded at a faster rate in vacuo. It should also be noted that the curves become more asymmetric with hold time.

4. Discussion

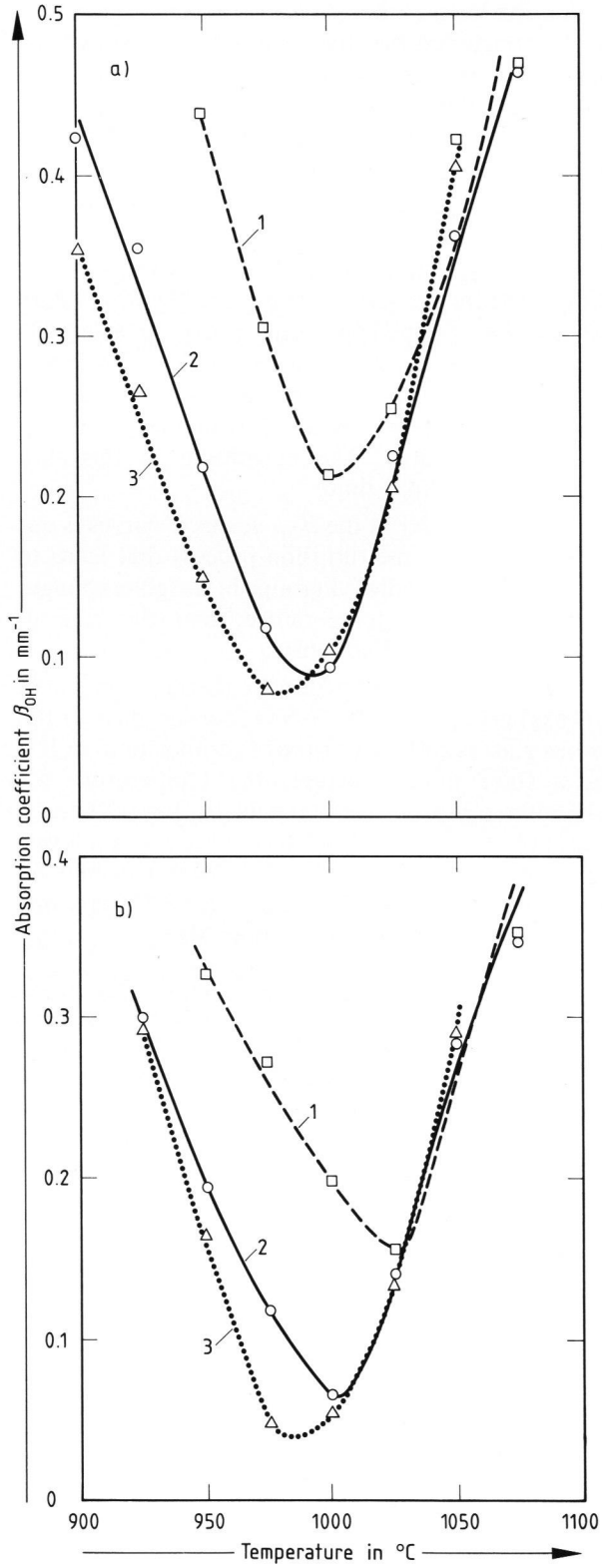
The removal of hydroxyl groups from porous glass involves condensation reactions between silanol (≡Si−OH) and also boranol (=B−OH) groups in the hydrated glass. According to Little and Mathieu [4], Wolf and Beyer [5], and others [6], such reactions are initiated at temperatures above 180 °C and continue uninteruptedly while the glass is still porous.

Both the rate of degassing (condensation reactions and removal of resulting molecular water) and the rate of consolidation of the structure increase with temperature, but since the former is determined largely by a diffusion process, it will change more slowly with temperature than the latter. At low temperatures, the degassing rate is too slow and at high temperatures the shrinkage process is too rapid

Table 1. Absorption coefficients β_{OH} of dry air and vacuum fired 96 % SiO_2 glass (by weight)

Temperature in °C	atmosphere	absorption coefficient β_{OH} in mm^{-1}		
		hold time in h		
		1 h	4 h	8 h
900	dry air	n.d.	0.424	0.353
925	= 180 ml/min	n.d.	0.355	0.265
950	at S.T.P.	0.440	0.217	0.150
975		0.309	0.118	0.078
1000		0.213	0.093	0.104
1025		0.255	0.225	0.206
1050		0.423	0.362	0.406
1075		0.470	0.464	n.d.
900	vacuum	n.d.	n.d.	n.d.
925	= 66.7 Pa	0.324	0.297	0.293
950		0.327	0.193	0.164
975		0.271	0.116	0.046
1000		0.197	0.064	0.053
1025		0.154	0.138	0.132
1050		0.289	0.282	0.290
1075		0.349	0.352	n.d.

n.d. = not determined



Figures 1a and b. Absorption coefficients β_{OH} of fired 96 % SiO_2 (by weight) glasses as a function of hold temperature. Hold times for curves 1, 2 and 3 equal 1, 4 and 8 h, respectively; a) fired in dry air, b) fired in vacuum.

compared to degassing. Hence, one can expect the β_{OH} values to be maximum for final glasses that had been subjected in the porous state to a low or a high hold temperature as depicted by the curves in figures 1a and b.

On the basis of the above-mentioned argument it can be concluded that there must be a hold temperature that assures maximum water removal. The minima in the curves enable one to locate this temperature. It corresponds to the optimum balance between diffusion and pore closure.

The data in table 1 show that vacuum firing is more effective in removing water from porous glass than air firing. This is chiefly due to speed up of water diffusion from the glass. However, low β_{OH} values also can be obtained by firing in dry air at atmospheric pressure, but it takes longer to do it. The effect of total pressure on optimum temperature for a given hold is indicated by a slight shift of the minima to lower temperatures. The magnitude of this shift decreases with hold time.

The asymmetry in the β_{OH} versus T curves is not unexpected since the diffusion process that leads to the reduction in hydroxyl groups in the glass changes more slowly with temperature than the rate of consolidation of the structure.

This study was confined to the thermal removal of hydroxyl groups from 96 % SiO_2 porous glass. If the porous glass is softer by virtue of composition, or if it has a finer pore structure, the temperature for maximum removal of water will be lowered for a given hold time since shrinkage will occur at a lower temperature. Consequently, such glasses cannot be dewatered to the same degree as a 96 % SiO_2 porous glass unless they have larger pore size.

5. Summary

The thermal removal of hydroxyl groups from porous glass is a function of temperature and hold time. The temperature for maximum removal of water decreases as hold time increases. This optimum temperature results from a balance in rates of water diffusion and glass sintering.

Increasing the total pressure of the atmosphere surrounding the porous glass during the degassing cycle decreases the net degassing rate.

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6. References

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