Flow and Diffusion Analysis on the Kinetics of Reduction of Fused Silica in Hydrogen

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The kinetics of the reduction of fused silica in hydrogen is studied from the viewpoint of the water vapor generation. The water vapor content in exhaust hydrogen gas is monitored at temperatures ranging from 700 to 1200°C. A model of the flow and diffusion of water vapor generated at the inner surface of a fused-silica tube in a hydrogen atmosphere is assumed for estimating the water vapor content. Then the reduction reaction rate constants are determined by the best fit to the measured water vapor concentrations at various temperatures in the range. Arrhenius plots of the rate constants give the activation energy to be approximately 85 kcal/mol, independent of gas flow rates and tube diameters, indicating that the reduction rate is reaction-limited. It is worth noting that this study demonstrates the validity of this numerical flow and diffusion analysis method on water vapor generation.   © 2001 Academic Press

Key Words: fused silica; reduction; activation energy; water vapor; hydrogen; reaction rate constant; Arrhenius plot; kinetics; numerical analysis; finite difference method.

INTRODUCTION

Heat treatments in the hydrogen atmosphere are utilized for various industrial applications, and process tubes are made from fused silica or various ceramics. Extensive studies on the reaction of silica with hydrogen have been made (1–3). Gardner examined the kinetics of the reduction of SiO_2 in hydrogen: he put a fused silica specimen in a muffle furnace and monitored its weight by the thermogravimetric method, obtaining the activation energy for the reduction reaction to be 85 kcal/mol (1).

Another standpoint for examining the reduction kinetics is the water vapor generation. This point of view has the advantage of analyzing the reduction reaction more directly than Gardner's one, because Gardner monitored the weight of silica, assuming that the only reaction that the silica sample participated in was the reduction by hydrogen. According to equilibrium thermodynamics, the concentration of water vapor generated by the reduction of fused silica in hydrogen is estimated to be, for example, approx. 30 ppm at 1200°C. Actually its concentration is not so high (as shown below), resulting in a problem of reaction kinetics. To analyze the contents of water vapor generated at elevated temperatures, a model of the flow and diffusion of the water vapor generated in hydrogen is needed in order to estimate the water vapor content.

In this study, we made real-time measurements of the water vapor generated using a hygrometer and applied the above model to the water vapor generation. From the water vapor contents measured, reduction reaction rate constants and activation energy are determined by best-fit numerical analysis based on the model.

EXPERIMENTAL PROCEDURES

Figure 1 shows a schematic diagram of the experimental apparatus. The contents of water vapor in ambient hydrogen gas, which flowed out through a fused-silica tube installed in a hot-wall-type furnace, were monitored by a Panametrics electric-capacitance-type hygrometer. The tube was made from fused glassy silica. In this experimental system, a flowmeter for ensuring a constant flow rate of the exhaust gas passing through the hygro-sensor chamber, regardless of the flow rate of the hydrogen gas through the silica tube, was installed. The water vapor contents in ambient nitrogen gas were also measured, to monitor the water vapor generation without hydrogen in our system. The dew point of the hydrogen gas used for the experiments was
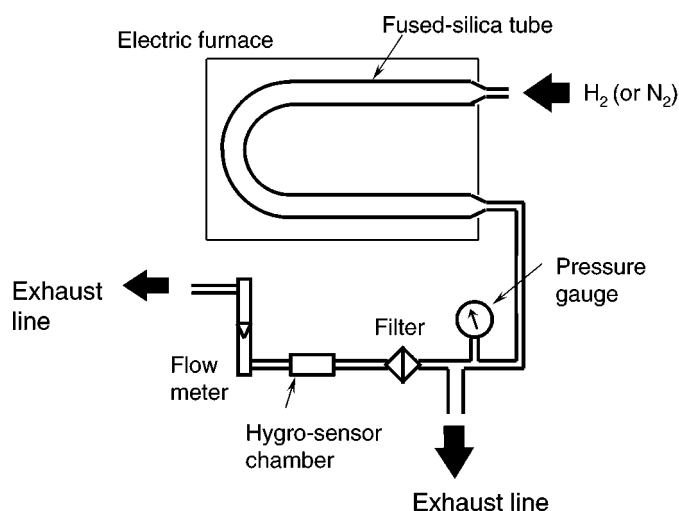
**FIG. 1.** Schematic diagram of the experimental apparatus.

approx. $-82°C$, i.e., water vapor concentration approx. 0.4 ppm, and that of the nitrogen gas was below $-85°C$, i.e., water vapor concentration < 0.2 ppm. The water vapor measurements were made at several temperatures ranging from 700 to 1200°C, as shown in Fig. 3. The ambient pressure was 1 atm. At each measurement, the temperature was kept constant for 1 h. To verify the common nature of the analyzed results, two silica tubes with different diameters were used for the experiments. For each tube, several kinds of flow rates were applied. These experimental conditions are shown in Table 1.

On the other hand, in order to utilize them for the numerical flow and diffusion analysis described in the next section, the equi-temperature lengths (deviation within $\pm 5°C$ around the set temperatures) in the tubes were measured in the nitrogen atmosphere by a Pt/Pt–Rh thermocouple.

ANALYZING PROCEDURES

In our experimental system, the reduction reaction by hydrogen is supposed to occur at the inner surface of a fused-silica tube, such as

$$SiO_2 + H_2 \xrightarrow{k} H_2O + SiO, \qquad [1]$$
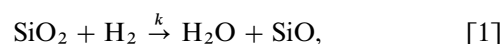
where k is the reaction rate constant. The production rate dC/dt of H_2O is given as

$$dC/dt = kP(H_2), \qquad [2]$$

where $P(H_2)$ is the vapor pressure of hydrogen, and C is the concentration of water vapor in hydrogen generated by reaction [1]. Since the measured concentration of water vapor is much lower than its equilibrium concentration (30 ppm), as shown below, the reverse reaction is negligible.

The water vapor generated at the inner surface of the silica tube flows through the tube with the ambient hydrogen gas. In the silica tube, diffusion of the water vapor must occur as well. Thus, the diffusion and flow equation of the water vapor in the tube is expressed as

$$\left(D\frac{\partial^2}{\partial r^2}C + \frac{D}{r}\frac{\partial}{\partial r}C + D\frac{\partial^2}{\partial x^2}C\right) + \frac{\partial}{\partial x}(C \cdot u) = \frac{\partial}{\partial t}C, \quad [3]$$
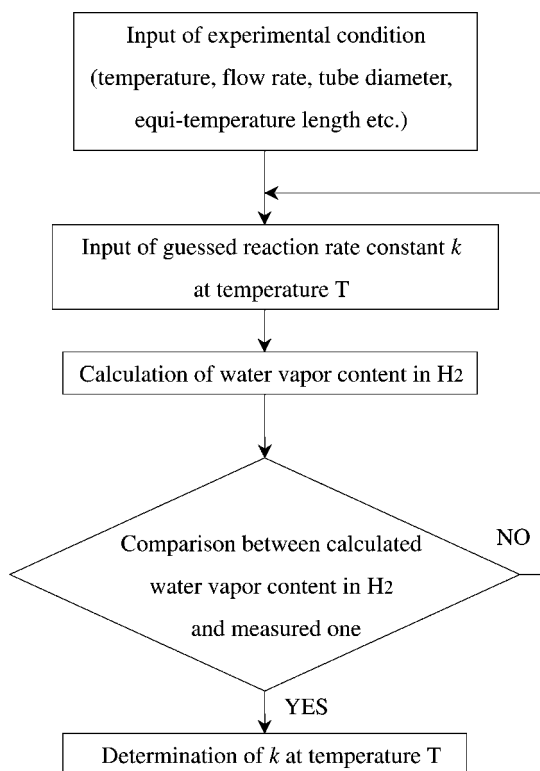
where r and x are the radial and axial coordinates within the tube, respectively, and D is the diffusion coefficient of water vapor in hydrogen (4). According to Arnold, the diffusion coefficients are estimated to be 10.23 and 13.1 at 1000°C and 1200°C, respectively (5). That is, D only changes a little in the temperature range 1000–1200°C. By the above numerical calculation, we ascertain that k is little affected by the D variation. In our work $D = 13.1$ cm^2/s is used. The radial distribution, $u(r)$, of the flow velocity of the water vapor in the tube is assumed as a parabolic form such as

$$u(r) = u_0\{1 - (r/a)^2\}, \qquad [4]$$

where a is the radius of the tube, and u_0 is the flow rate divided by the cross section of the tube (6). In Eq. [3], the three terms in parentheses on the left side are due to the diffusion of the water vapor, and the final term on the same side is due to its flow.

TABLE 1
Experimental Conditions and Analyzed Results

Silica tube inner diameter (cm)	Flow rate (L/min)	Equi-temperature length (cm)	Water vapor concentration C generated at 1200°C (ppm)	Reaction rate k at 1200°C (mol/cm$^2\cdot$s$\cdot$atm)	Activation energy E_a (kcal/mol)
4.15	2	54	2.57	5.15×10^{-12}	86.4
5.80	2	35	2.85	6.48×10^{-12}	80.2
5.80	4	32	0.92	4.40×10^{-12}	87.4
5.80	5	31	0.86	5.30×10^{-12}	86.2

FIG. 2. Flow chart for the fitting procedure to determine the reaction rate constants k. YES and NO mean agreement between the measured and calculated water vapor contents in hydrogen and disagreement between them, respectively.

FIG. 3. Measured water vapor contents in hydrogen and nitrogen, for the case of a flow rate of 2 L/min and a silica-tube inner diameter of 4.15 cm. Solid lines and closed lozenges represent the annealing temperature and observed water vapor contents, respectively. (a) Annealing in hydrogen, and (b) annealing in nitrogen.
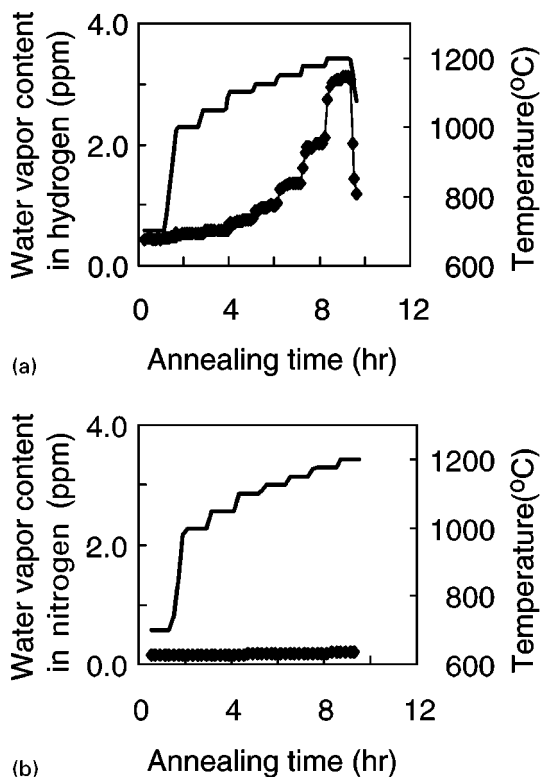
At several temperatures between 1000 and 1200°C, the reaction rate constants k were determined by the best fit to the water vapor concentration C, based on Eqs. [3] and [4]. The flow chart for the fitting procedure is shown in Fig. 2. The value C was obtained by subtracting the water vapor content value measured at 700°C from that measured at each measurement temperature. In the fitting procedures, each calculation of the water vapor concentration from the guessed reaction constant was performed by the finite difference method. The calculations were carried out using a personal computer. Then Arrhenius plots of k were made, to obtain the activation energy E_a of reaction [1], which is defined by the Arrhenius equation

$$k = A \exp(-E_a/k_B T), \qquad [5]$$

where A is a constant and k_B is the Boltzmann constant (7).

RESULTS AND DISCUSSION

Figure 3 shows the measured water vapor contents in hydrogen and nitrogen, for the case of a flow rate of 2 L/min and a silica-tube inner diameter of 4.15 cm. The water vapor content in hydrogen increases with annealing temperature.

Especially at 1200°C, the increase is significant. However, little water vapor is generated in the nitrogen annealing. Arrhenius plots of the rate constants k obtained for the above case are shown in Fig. 4. There is an excellent lin-
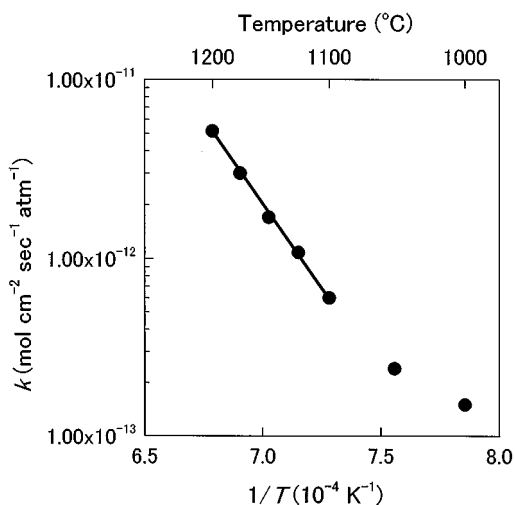
FIG. 4. Arrhenius plots of the rate constants k (flow rate = 2 L/min and inner diameter of the silica tube = 4.15 cm).

earity in the temperature range 1100–1200°C. From the Arrhenius plots in the temperature range, the activation energy is derived to be 86.4 kcal/mol. We used only the measured concentrations of water vapor in the higher temperature range (1100–1200°C) to calculate the activation energy. This is because the measured concentrations in the lower temperatures are so low that the reliability of these measurements is not so good.

In Table 1, the measured water vapor concentrations C in the exhaust hydrogen gas at 1200°C, the reduction reaction rate constants k at 1200°C determined from the water vapor concentration, and the activation energy E_a obtained from the Arrhenius plots are summarized under the different experimental conditions such as the gas flow rates and the inner diameters of the fused-silica tubes. The equi-temperature length measured at 1200°C for each experimental condition is also shown in the table. (The length is almost independent of the temperature.)

From Table 1, it is evident that the reduction reaction rate constant k at 1200°C is approx. 5.3×10^{-12} mol cm^{-2} s^{-1} atm^{-1} and the activation energy E_a is approx. 85 kcal/mol, independent of the gas flow rates and the tube diameters, although the water vapor content increases with the gas flow rate. This indicates that the reduction reaction rate is reaction-limited. The measured activation energy is almost the same as that by Gardner (1), showing the validity of our analyzing procedures. In contrast to Gardner's work, our study presents a successful example of the kinetic analysis on the gaseous product using a flow and diffusion model.

CONCLUSION

The kinetics of the reduction of fused silica in hydrogen is studied from the viewpoint of water vapor generation. The water vapor content in exhaust hydrogen gas is monitored at temperatures ranging from 700 to 1200°C. From the measured water vapor contents, the reaction rate constants k are determined by best-fit numerical analysis, which is based on a model of the flow and diffusion of water vapor generated at the inner surface of a fused-silica tube in a hydrogen atmosphere. From Arrhenius plots of k, the activation energy E_a is obtained to be approx. 85 kcal/mol, independent of gas flow rates and inner diameters of the tubes. This indicates that the reduction reaction rate is reaction-limited. It is noteworthy that this study demonstrates the validity of the numerical analysis method on water vapor generation.

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