Evaporation Behavior of SiO₂ in N₂-O₂-H₂O Atmospheres*

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In order to clarify the influence of water vapor on evaporation and crystallization of an amorphous SiO₂ scale formed on SiO₂-formers, fused silica was exposed for up to 49 h at 1373–1673 K in N₂-O₂-H₂O atmospheres. The water vapor concentration was regulated to 19.6 and 46.7% (vol%). Under conditions of low water vapor concentration, the mass change in the fused silica was negligible. On the other hand, the mass linearly decreased with the duration of exposure under high water vapor concentration. From the temperature dependence of the evaporation rate, it was speculated that the main volatile species were Si(OH)₄ and SiO(OH)₂ in N₂-H₂O and N₂-O₂-H₂O, respectively. Moreover, although crystallization of fused silica was observed in both atmospheres, air and N₂-O₂-H₂O, the rate of crystallization in the N₂-O₂-H₂O atmosphere was much higher than that in air. These results indicate that crystallization is accelerated by the presence of water vapor.

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1. Introduction

Silicides and ceramics, such as SiC, Si₃N₄, and MoSi₂, have been cited as candidate materials for application to such high temperature parts, and these form a SiO₂ scale which functions as an excellent protective oxide scale in high-temperature oxidizing atmospheres. However, in atmospheres containing water vapor, the oxidation resistance of the SiO₂ scale is poor, and this leads to recession of the substrate. The reasons for the poor oxidation resistance, based mainly on the degenerative factor of water vapor, are probably:

(1) evaporation of the SiO₂ scale due to the reaction of the SiO₂ scale and water vapor react, and

(2) crystallization of the SiO₂ scale by water vapor, leading to cracking and spalling in the SiO₂ scale due to the volume change accompanying crystallization. However, there have been few research reports^{1–3)} concerning the evaporation behavior and crystallization of a SiO₂ scale in atmospheres containing water vapor, and the details of this behavior are still unclear.

In this study, in order to examine fundamentally the evaporation and crystallization of a SiO₂ scale in an atmosphere containing water vapor, we performed high temperature exposure experiments on a fused SiO₂ substance in N₂-O₂-H₂O atmospheres, studied evaporation behavior from the mass change, and investigated the effect of water vapor on the crystallization of amorphous SiO₂.

2. Background

2.1 Evaporation of SiO₂ by reaction with water vapor

It is known that a SiO₂ scale forms volatile hydroxides or oxyhydroxides in atmospheric pressure environment containing water vapor.^{1–3)} In general, the following reactions are considered to be most likely to occur.¹⁾

According to recent studies,^{1,4,5)} it has been reported that the species SiO(OH) and Si(OH)₄ are predominant volatile species in atmospheric pressure environment. On the other hand, the evaporation species Si₂O(OH)₆ is a preferential substance under very high water vapor pressure (~10⁷ Pa) conditions.³⁾

2.2 Crystallization of amorphous SiO₂ scale

Basically, a SiO₂ scale formed on SiO₂-forming materials such as SiC, Si₃N₄ and silicides is amorphous, and its amorphous quality is a factor in the highly protective nature of the SiO₂ scale. However, as the temperature increases, the SiO₂ scale crystallizes and undergoes a phase change leading to volumetric shrinkage and loss of deformability, so its protective qualities degrades. Although it is known that crystallization is promoted in an atmosphere containing water vapor, there are few reports on the effect of water vapor on the crystallization of an amorphous SiO₂ scale,^{1–3)} and the details are not clear. It is thought that an understanding of crystallization is important in elucidating the protective qualities of a SiO₂ scale.

3. Experimental Method

In this experiment, fused silica (Good Fellow Co. Ltd.) was used as a sample. After cutting the sample to a size of 10 × 10 × 2 (×10⁻³ m), mechanical polishing to #1500 was performed. Then, buffing was carried out with 1-μm diamond paste, and ultrasonic cleaning was performed in ethanol.

Exposure tests were performed in N₂-H₂O or (N₂-20%O₂)-H₂O atmospheres at temperatures of 1373–1673 K for exposure time of 3.6–176.4 ks. In the present study, as a fundamental study for many combustion systems such as incinerator and gas turbine, fused SiO₂ was exposed to the atmospheres with high or low water vapor concentration. The water vapor concentration was controlled by volume % to

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Fig. 1 Change in mass of fused silica with time for SiO₂ during exposure at 1473 K in (a) N₂-H₂O and (b) N₂-O₂-H₂O atmospheres.

Fig. 2 Mass loss showing the volatility of SiO₂ at 1473-1673 K in (a) N₂-46.7%H₂O and (b) (N₂-20%O₂)-46.7%H₂O.

19.6 or 46.7% by setting the temperature of a water bath to 333 K or 353 K. The gas mass flow at this time was 8.33×10^{-6} m³/s at room temperature. Converting this flow rate to a linear velocity at 1373–1673 K, this corresponds to 0.06–0.07 m/s.

The mass change due to evaporation was obtained by measuring the mass of a sample before and after a predetermined exposure time with a microbalance. The X-ray diffraction method (XRD) and a scanning electron microscope (SEM) were used for identification of crystal structure and observation of a cross-section.

4. Results and Discussion

4.1 Effect of water vapor concentration on evaporation behavior of SiO₂

The effect of water vapor concentration on the evaporation behavior of fused SiO₂ at 1473 K in N₂-H₂O and N₂-O₂-H₂O is shown in Fig. 1. In N₂-19.6%H₂O and (N₂-20%O₂)-19.6%H₂O, the mass loss can be ignored, but in N₂-46.7%H₂O and (N₂-20%O₂)-46.7%H₂O, a linear mass loss with time is observed. The same evaporation behavior was obtained also at 1573 K and 1673 K. It is speculated that this mass loss results from evaporation due to the reaction of water vapor with SiO₂. Therefore, the result obtained from Fig. 1 shows that the evaporation of SiO₂ is promoted in an atmosphere with a high water vapor concentration. However,

the reason why the mass loss in 19.6%H₂O atmospheres is negligibly small is not clear.

4.2 Evaporation behavior of SiO₂ under a high water vapor concentration

The time dependency of the mass change in N₂-46.7%H₂O and (N₂-20%O₂)-46.7%H₂O at 1473-1673 K is shown in Fig. 2. In both N₂-46.7%H₂O and (N₂-20%O₂)-46.7%H₂O, a linear mass loss with time is observed at all temperatures. The evaporation rates calculated from the slope of the lines are shown in Table 1. These values are in good agreement with the evaporation rate in 50%O₂-50%H₂O at 1573 K reported by Opila *et al.*¹⁾ These results indicate that the oxygen partial pressure doesn't have strong effect on the evaporation of SiO₂.

4.3 Estimation of evaporation species based on free evaporation model

As the gas flow rate is very small under the present experimental conditions, it is assumed that a gas boundary layer is not formed. Then, the evaporation behavior can be considered to be based on the free evaporation model (Langmuir equation) wherein the evaporation rate is given by the following equation:

$$k_1 = P / \sqrt{2\pi MRT} \quad (4)$$

Herein, k_1 is the evaporation rate of the evaporation species, P

Table 1 Linear evaporation rate, k_1 , of fused silica in N_2 -46.7% H_2O and $(N_2$ -20% O_2)-46.7% H_2O atmospheres, comparing with that of calculated for $Si(OH)_4$ and $SiO(OH)_2$.

Temp. (K)	k_1 (kg/m ² s)			
	N_2 -46.7% H_2O	N_2 -20% O_2 -46.7% H_2O	$Si(OH)_4$	$Si(OH)_4$
1473	1.87×10^{-9}	1.10×10^{-9}	4.37×10^{-10}	5.16×10^{-10}
1573	2.24×10^{-9}	1.87×10^{-9}	6.30×10^{-10}	1.94×10^{-9}
1673	2.68×10^{-9}	1.22×10^{-8}	7.57×10^{-10}	5.84×10^{-9}

Fig. 3 Variation of $Si(OH)_4$ and $SiO(OH)_2$ pressures with temperature in water vapor pressure of 4.7×10^4 Pa which were calculated from the results of Hashimoto⁴⁾ and Krikorian.⁶⁾

Fig. 4 Linear evaporation rate for fused silica in N_2 -46.7% H_2O and $(N_2$ -20% O_2)-46.7% H_2O . Dashed lines show evaporation rate of $Si(OH)_4$ and $SiO(OH)_2$.

is the equilibrium vapor pressure of the evaporation species, M is the molecular weight of the evaporation species, R is the gas constant and T is the absolute temperature.

As stated previously, in atmospheres containing water vapor, the important evaporation species are thought to be $Si(OH)_4$ and $SiO(OH)_2$. The vapor pressures of $Si(OH)_4$ and $SiO(OH)_2$ under these conditions are estimated as approximately 0.1–1 Pa at 1373–1773 K from the data of Hashimoto⁴⁾ and Krikorian.⁶⁾ Therefore, the evaporation rate of the evaporation species in the free evaporation model was calculated using the vapor pressure of $Si(OH)_4$ and $SiO(OH)_2$ under the partial water vapor pressure of 5×10^4 Pa by Hashimoto and Krikorian shown in Fig. 3. As a result, the evaporation rates of $Si(OH)_4$ at 1473 K, 1573 K and 1673 K were calculated respectively as 4.4×10^{-10} , 6.3×10^{-10} and 7.6×10^{-10} kg/m²s. Also, the evaporation rates of $SiO(OH)_2$ at 1473 K, 1573 K and 1673 K were calculated respectively as 5.2×10^{-10} , 1.9×10^{-9} and 5.8×10^{-9} kg/m²s. These evaporation rates are shown together with the evaporation rates in this experiment in Table 1. Comparing the evaporation rates at each temperature, it is seen that the evaporation rates obtained from this experiment are within about one order of magnitude of the evaporation rates of each evaporation species, and there is good coincidence.

The temperature dependency of the evaporation rates of $Si(OH)_4$ and $SiO(OH)_2$ obtained in this experiment is shown in Fig. 4. The activation energies of evaporation from the slope of the line were 78.2 kJ/mol in N_2 - H_2O and 253.5 kJ/mol in N_2 - O_2 - H_2O . On the other hand, the activation energies of evaporation of $Si(OH)_4$ and $SiO(OH)_2$ calculated from the data of Hashimoto⁴⁾ and Krikorian⁶⁾ were respectively 52.4 kJ/mol and 248.6 kJ/mol. Thus, the activation energy of evaporation in N_2 - H_2O coincided well with the activation

energy of $Si(OH)_4$, and the activation energy of evaporation in N_2 - O_2 - H_2O coincided well with the activation energy of $SiO(OH)_2$. This suggests that in N_2 - H_2O , the reaction (1) (reaction producing $Si(OH)_4$) occurs, and in N_2 - O_2 - H_2O , the reaction (2) (reaction producing $SiO(OH)_2$) occurs.

4.4 Effect of water vapor on crystallization of amorphous SiO_2

When a XRD analysis of a specimen after an exposure test was carried out, a cristobalite peaks were observed at 1573 K and above in air, while they were observed at 1473 K and above in an atmosphere containing water vapor, confirming that crystallization started at 1573 K and 1473 K, respectively. In other words, in an atmosphere containing water vapor, crystallization of SiO_2 appears to start at a temperature about 100 K lower than in air. Figure 5 shows a cross-sectional SEM image of a sample exposed in air and in $(N_2$ -20% O_2)-46.7% H_2O atmosphere at 1573 K for an exposure time of 3.6–176.4 ks. In both atmospheres, cracks were observed in a surface area of specimen due to a volume change accompanying crystallization. It is seen that the area with cracks increases with exposure time. This shows that crystallization progresses from the surface towards the interior with exposure time. Also, comparing the crystallization area in air and an atmosphere containing water vapor at each time, it is seen that the area is larger in the atmosphere containing water vapor. This means that crystallization is promoted by water vapor. From observations of the crystallization range formed in $(N_2$ -20% O_2)-46.7% H_2O at 1473–1673 K, the thickness from the surface of the crystallization area was measured, and this was plotted against exposure time in Fig. 6. At all temperatures, crystallization proceeds almost linearly with time, and the crystallization rate increases

Fig. 5 Cross-sectional microstructure of fused silica exposed at 1573 K in (a) air and (b) (N₂-20%O₂)-46.7%H₂O.

Fig. 6 Growth rate of crystallized layer in fused silica in (N₂-20%O₂)-46.7%H₂O.

linearly with temperature rise. The crystallization rates calculated from the slope of the line are summarized in Table 2. The crystallization rate was $1.7 - 13.1 \times 10^{-10}$ m/s at 1473–1673 K, and was about 4 times higher than in air at 1573 K.

5. Conclusion

Fused SiO₂ was exposed in various N₂-O₂-H₂O atmospheres in a temperature range of 1373–1673 K. The effect of water vapor on evaporation behavior and crystallization of amorphous SiO₂ was examined, and the following results were obtained.

- (1) The evaporation of SiO₂ became more marked from 1473 K.
- (2) The evaporation of SiO₂ was promoted in an

Table 2 Linear crystallization rate, r_c , determined from thickness of crystallization area of amorphous SiO₂ in (N₂-20%O₂)-46.7%H₂O atmosphere, comparing to that in air.

Temp. (K)	Crystallization rate r_c (m/s)	
	N ₂ -20%O ₂ -46.7%H ₂ O	Air
1373	No crystallization	No crystallization
1473	1.7×10^{-10}	No crystallization
1573	4.7×10^{-10}	1.1×10^{-10}
1673	13.1×10^{-10}	

atmosphere with a high water vapor concentration.

- (3) The mass of SiO₂ decreased linearly with time.

(4) It is conjectured that in a N₂-H₂O atmosphere, an evaporation reaction producing Si(OH)₄ occurs, and in a N₂-O₂-H₂O atmosphere, a reaction producing SiO(OH)₂ occurs.

(5) In an atmosphere containing water vapor, crystallization occurs at a temperature about 100 K lower than in air.

(6) The crystallization rate in an atmosphere containing water vapor is about $1.7 - 13.1 \times 10^{-10}$ m/s at 1473–1673 K.

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