Oxidation Behavior of Porous Silicon Carbide Ceramics under Water Vapor below 1000°C and Their Microstructural Characterization

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1000°C 以下の水蒸気環境下での多孔質炭化ケイ素の酸化挙動と微細構造評価

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The water vapor oxidation behavior below 1000°C for porous silicon carbide ceramics with and without additive alumina was investigated. The relationship between the microstructure of porous SiC and vapor oxidation was examined. The varied microstructures, such as pore size and particle size were found to affect the water vapor oxidation behavior of porous SiC. The porous SiC without alumina showed a good stability for water vapor. This was due to the microstructure of large particles and pores in the undoped SiC. In contrast, the porous SiC with alumina after vapor oxidation showed the microstructural changes such as the increase of pore size and particle size, and the disappearance of fine particles, because the porous SiC with alumina was composed of fine particles and small pores.

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1. Introduction

Porous silicon carbide (SiC) has been widely utilized as catalyst supports,^{1)–3)} the membrane support^{4)–6)} of hydrogen production and diesel particulate filter (DPF)⁷⁾ because of its good thermal shock resistance and low thermal-expansion coefficient as well as its excellent mechanical and chemical stabilities. Hydrogen production by ceramic membrane is expected as a high efficiency method, and DPF is a fundamental component to eliminate particulate in exhaust gas from diesel cars. Porous SiC is a promising material for membrane support or DPF, because the stability under a high temperature water vapor is required for these components.

For hydrogen production by porous SiC membrane reactor, the production reaction by water vapor and natural gas below 1000°C is attempted.^{8),9)} Also, the temperature of DPF exposed for gases and water vapor is below 1000°C. As seen from the previous work about the oxidation of SiC by water vapor, many studies have reported a dense SiC and temperature above 1200°C.^{10)–14)} However, the studies about stability of porous SiC under water vapor below 1000°C have not been reported to date, in our knowledge. The porous ceramic is generally composed of particle, pore and neck area among particles, which microstructures can be controlled by sintering routes such as partial liquid phase and recrystallization.^{4),5),15)–17)} Under a high temperature water vapor, the microstructures of porous SiC may affect its stability. In this paper, we report the relationship between the microstructure of porous SiC and the stability under the water vapor below 1000°C.

2. Experimental procedure

High purity β -SiC (Ibiden Co., Ltd.) powder with an average particle size of 0.30 μm and a specific surface area of 20.0 m^2/g was used as a raw material. Also the additive, α - Al_2O_3 (Taimei Chemicals Co., Ltd.) with an average particle

size of 0.20 μm was used. The mixtures with weight ratios of $\text{Al}_2\text{O}_3/\text{SiC}=0/100$ and 4/96 were blended in ethanol for 1 h using a planetary mill with a SiC pot and SiC balls. After mixing, the slurry was dried with a rotary evaporator and a vacuum oven at 110°C for 4 h, and screened through a 110 mesh sieve. The powder compacts were formed into a disk shape without any binder by using a steel mold at 40 MPa, and then treated with a cold isostatic press (CIP) at 400 MPa. The green bodies were placed in a capped graphite crucible and sintered at 1800°C for 2 h under an Ar gas flow. Hereafter, these are referred as SC and SCA, respectively, according to additive. The properties of the obtained porous SiC specimens are illustrated in Table 1.

The apparent densities of obtained porous SiC were measured by the Archimedes method. The specific surface area was characterized by nitrogen adsorption/desorption measurements (Yuasa Ionics Inc., Autosorb, Osaka). The specific surface area was determined from a BET (Brunauer, Emmet and Teller) analysis in the P/P_0 range of 0.05–0.30 using a molecular cross sectional area for N_2 of 0.163 nm^2 and multi points (11 points).

The water vapor oxidation test was performed using a Corrosion Testing Machine at the Japan Ultra High Temperature Materials Research Center. The oxidation tests were performed at 600°C or 1000°C and the holding period was 100 h. Nitrogen gas flowed to the above testing temperature

Table 1. Properties of Porous Specimens

Sample	Density (g/cm^3)	Porosity	BET particle size (μm)
SC	2.0	37	0.9
SCA	2.1	34	0.3

Table 2. Specific Weight Change (mg/cm²), Conversion Rate and Density of the Specimens After Vapor Oxidation

	Sample			
	SC		SCA	
Oxidation temperature (°C)	600	1000	600	1000
Specific weight gain (mg/cm ²)	0.32	3.81	0.68	13.6
Conversion (%)	0.3	2.6	0.5	10.4
Density (g/cm ³)	2.0	2.0	2.1	2.1

and then a mixed gas of N₂ and H₂O was introduced for the holding period. The partial pressure of water vapor was kept at 1/3 (N₂/H₂O) under 1 atm and the gas flow rate was 100 ml/min, where the flow rate of nitrogen gas (25 ml/min) was controlled by a flow meter and the flow rate of water vapor (75 ml/min) was controlled by the temperature of a water bubbler to show its vapor pressure (0.75 atm).

X-ray photoelectron spectroscopy (XPS) was used for the structural investigation of the surface of the specimens before and after the water vapor oxidation test. The measurements were operated at around 1.3×10^{-8} Pa and using Mg K α radiation. The C (1s) spectra as an internal reference (284.6 eV in hydrocarbon) were used as the calibration of the binding energy. The microstructures before and after the water vapor oxidation test were observed using a scanning electron microscopy (SEM; JEOL-6330F, Tokyo). The pore size distributions before and after oxidation were measured by a mercury porosimetry (Yuasa Ionics Inc., PoreMaster-GT, Osaka) in the range of 6.1 nm–426 μ m.

3. Results and discussion

Table 2 shows the specific weight changes, conversion rate and density of the specimens after vapor oxidation. The weight gain of the SCA specimen after vapor oxidation was larger than that of the SC specimen. In addition, a higher oxidation temperature was found to result in a larger weight gain. The weight gain is considered to be according to the following Eq. (1):

The conversion rate from SiC to silica could be calculated by this equation. The complete oxidation to SiO₂ results in the weight gain of 50 mass%. Thus, the conversion rate to silica can be worked out by the measured weight gain (mass%)/the weight gain of complete oxidation (50 mass%). From these results, the conversion of the SCA was around 10% and larger than that of the SC. However, the conversion rate of the SCA was not found to be of such a large value to significantly change the density.

Figure 1 shows the FE-SEM micrographs of the fractured surface of the SC (Figs. 1 (a)–(c)) and SCA (Figs. 1 (d)–(f)) specimens before and after vapor oxidation. In (a) and (d) micrographs, the particle size and pore size could be varied by the addition of alumina, which is due to the different mass transfer in sintering. The detail of the process strategy to control the microstructure of porous SiC has been reported elsewhere.⁶ It can be clearly seen that the microstructure of the SCA dramatically changes with the higher oxidation temperature, while that of the SC does not change significantly, even after oxidation at 1000°C.

In the SCA, the morphological changes were more clearly observed in the enlarged SEM photographs, shown in **Fig. 2** (the SCA (a) before and (b) after vapor oxidation at 1000°C). The fine particles below 0.1 μ m disappeared (indicated by marking), and the pore size (indicated by arrow) and particle size increased by the oxidation test.

The changes of particle size before and after vapor oxidation can give important information to further understand the vapor oxidation of porous SiC. The SC and SCA possessed 0.9 and 0.3 μ m in average particle size, respectively (see Table 1), which could be estimated by the following Eq. (2):

$$R = \frac{6}{\text{SSA} \times d} \quad (2)$$

where R , SSA and d indicate particle size, BET specific surface area and density. Although we measured the surface area of the specimen after the oxidation test, the precise particle size after oxidation cannot be calculated because the theoretical density of the specimen after oxidation was not clear. However, its density should be in the range of 3.2–2.2 (silicon carbide–silica). The particle size after oxidation could be calculated to be 0.9–1.0 μ m for the SC and 0.4–0.7 μ m for the SCA. Here, when the difference of the particle size before and after vapor oxidation is considered, that means the thickness of a covered silica layer formed on the surface of the SiC particle. The covered layer was calculated to be less than 0.1 μ m for the SC and 0.1–0.4 μ m for the SCA in the thickness. Thus, these estimations also suggest that the fine particles below 0.1 μ m are completely converted.

Figure 3 shows the pore size distribution of the SC and SCA before and after vapor oxidation. It can be seen that the pore size of the SC did not significantly change, while that of the SCA slightly increased and the small pore less than 0.1 μ m was almost found to disappear.

Here, we want to suggest the following hypothesis for the morphological changing by vapor oxidation. During the vapor oxidation test, the surface of the SiC particle is oxidized, and then the silica layer is generated by Eq. (1). Also, some fine SiC particles below 0.1 μ m are completely oxidized into silica. The silica layer on the surface of the particle or the formed silica particle may partially accompany with Si–OH (silanol) groups under a high temperature vapor,^{18)–20)} according to Eq. (3):

Since the viscosity of silica generally decreases with an increase of silanol content,¹⁹⁾ the surface silica layer of low viscosity may gradually gather around neck part by surface tension or the coalescence among oxidized low-viscous fine particles may occur. These should cause the increase of the particle size, pore size and neck part, and the disappearance of fine particles, which are observed by the results of FE-SEM and mercury porosimetry.

Figure 4 illustrates the Si(2p) XPS spectra of the SC and SCA before and after vapor oxidation. As seen from the Si (2p) spectra, the peaks due to silicon carbide for the specimens before oxidation, silicon oxycarbide after oxidation at 600°C and silica for ones after oxidation at 1000°C were detected, respectively.^{21)–23)} Though the conversion from SiC to oxycarbide was monitored at 600°C, the complete conversion to silica at this temperature did not be observed at surface detected by XPS. In addition, silica and oxycarbide species can accompany Si–OH group in their terminal site, which may suggest the substitution by water vapor.

Table 3 summarizes the surface compositions (oxycarbide

Fig. 1. FE-SEM micrographs of the specimens before (a, d) and after vapor oxidation at 600°C (b, e) and at 1000°C (c, f) for SC (a, b and c) and SCA (d, e and f) specimens, respectively.

stoichiometry) of the specimens after oxidation, calculated by the ratio of the Si (2p) deconvoluted peak area. These could be calculated by the following 4 and 5 equations, where x and F ($\text{SiC}_{4-x}\text{O}_x$) indicate the bonding number of Si-O ($x=0-4$) and the ratio of peak area for silicon carbide ($x=0$), oxycarbide ($x=1-3$) and silica ($x=4$). Then, the surface composition could be worked-out by the sum of the ratio of peak area and their division by the coordination number of oxygen or carbon.

$$\text{O/Si} = \frac{\sum_{x=0}^4 F(\text{SiO}_x\text{C}_{4-x})x}{2} \quad (4)$$

$$\text{C/Si} = \frac{\sum_{x=0}^4 F(\text{SiO}_x\text{C}_{4-x})(4-x)}{4} \quad (5)$$

Though the SCA showed the larger weight change by oxidation, the difference of the surface composition between SC and SCA was not significantly seen. Namely, this suggests that the rate of oxidation of SiC may be nearly equal for both

specimens. However, many fine particles in the SCA were oxidized, resulting in the larger weight changes.

4. Conclusion

In this work, the vapor oxidation of porous silicon carbide below 1000°C was investigated. The microstructure of porous specimens was found to closely relate with the oxidation behavior.

The following important results were obtained.

(1) The porous SiC without additive showed a good stability for water vapor. The weight, the pore size and the particle size were not significantly changed by vapor oxidation.

(2) In the porous silicon carbide with additive, the microstructural changes were observed. The disappearance of fine particles below 0.1 μm , and the increase of pore size and particle size were monitored by the vapor oxidation test.

(3) The complete conversion to silica at 600°C was not monitored in all specimens, which was confirmed by X-ray photoelectron spectroscopy.

Fig. 2. High magnification FE-SEM observations of the SCA before (a) and after (b) vapor oxidation at 1000°C.

Fig. 3. Pore size distribution of the specimens before and after vapor oxidation.

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Fig. 4. Si (2p) spectra of the specimens before and after water vapor oxidation.

Table 3. Surface Composition of the Specimens After Vapor Oxidation

Sample	Surface composition (Si2p)	
	600°C	1000°C
SC	SiC _{0.53} O _{0.94}	SiO ₂
SCA	SiC _{0.52} O _{0.95}	SiO ₂

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