High Temperature Behaviors of Silicon Carbide in Impurity-Controlled Helium Environment

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1. Introduction

Silicon carbide (SiC) is a matrix material of the SiC_f/SiC composite used as a control rod sheath in VHTR. During normal operation of VHTR, SiC goes through the active or passive oxidation by the reaction with the impure helium coolant depending on partial pressure of oxidants. Therefore, this study focuses on the oxidation behaviors of SiC in the impurity-controlled helium environment to observe the effect of impurity gases on the active or passive oxidation.

2. Experimental

Chemical vapor deposited (CVD) β-SiC was oxidized at 950°C in the impurity-controlled helium environment that contained H_2, CO, H_2O, and CH_4, as listed in Table I. Impurity gases such as H_2, CO, and CH_4 were controlled individually using mass flow meter (MFC). O_2 was removed by the reaction with graphite at 900°C. Impurity concentrations were measured in real time during oxidation by gas chromatography (GC). Total gas flow was 50 sccm.

Table I: Composition of Impurities in the Helium Gas

	He	H_2	H_2O	CO	CH_4
Gas Composition (Pa)	Bal.	20	0.02 -0.1	5	2

3. Results and Discussion

Active oxidation of SiC is generally characterized by a weight loss caused by the production of SiO(g). Passive oxidation is characterized by a weight gain caused by the formation of SiO_2(s) on the surface of SiC. However, weight changes of CVD β-SiC were barely measurable for up to 250 hours of oxidation in the impurity-controlled helium environment, and therefore surface analysis was performed to determine whether the active or passive oxidation occurs.

Fig. 1 shows AFM images of as-received and oxidized CVD β-SiC. Minute scratches were observed in both as-received and oxidized specimens because the reaction rate between CVD β-SiC and environment is extremely low. The root mean square surface roughness of oxidized one was slightly increased from 2.057 nm to 2.942 due to the growth of oxide scale by the passive oxidation.
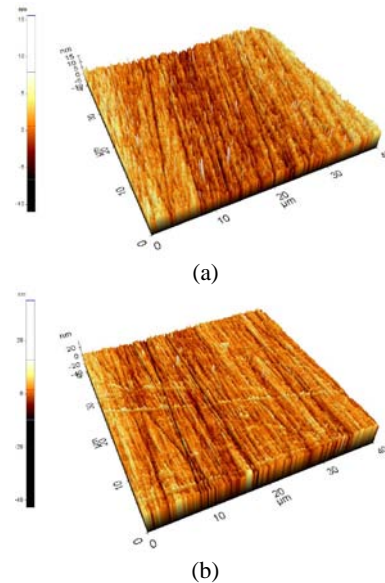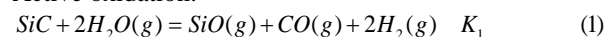

(a)

(b)

Fig. 1. AFM images of CVD β-SiC: (a) as-received and (b) oxidized for 250 hours at 950°C in the impurity-controlled helium.
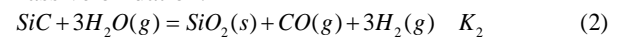
A XPS peak for Si $2p_{1/2,3/2}$ is composed of three components as shown in Fig. 2. The peak located at 100.5 eV is attributed to Si-C bonds of SiC. The peak located at 102.2 eV is attributed to Si-O bonds of SiO_xC_y(x+y=4). The peak located at 103.2 eV is attributed to Si-O bonds of SiO_2. Compared to Si $2p_{1/2,3/2}$ peaks for the as-received one as shown in Fig. 2(a), a Si-O peak intensity for SiO_2 formed in the impurity-controlled helium environment was increased considerably as shown in Fig. 2(b). On the other hand, a Si-O peak for SiO_xC_y almost disappeared. As the oxidation progressed, relative peak intensity of Si-O for SiO_2 and Si-C for SiC did not change as shown in Fig. 3. It implied that SiO_2 was formed at initial stage of passive oxidation and the oxidation rate is very slow at the steady state.

H_2O is a primary oxidant in the impurity-controlled helium environment. The oxidation of SiC in H_2O occurs via the reactions:

Active oxidation:
$$SiC + 2H_2O(g) = SiO(g) + CO(g) + 2H_2(g) \quad K_1 \quad (1)$$

Passive oxidation:
$$SiC + 3H_2O(g) = SiO_2(s) + CO(g) + 3H_2(g) \quad K_2 \quad (2)$$
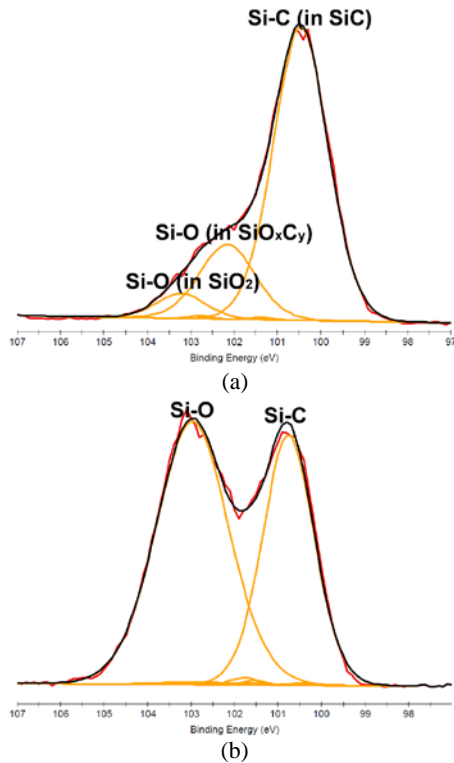
(a)

(b)

Fig. 2. XPS peaks of CVD β-SiC: (a) as-received and (b) oxidized for 250 hours at 950°C in the impurity-controlled helium.
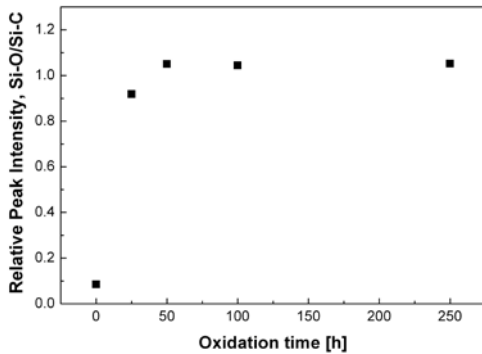

Fig. 3. Relative peak intensity of Si-O in SiO$_2$ and Si-C in SiC after oxidation at 950°C in the impurity-controlled helium.

Since the reaction between SiC and H$_2$O has a low activation energy, the oxidation occurs rapidly when H$_2$O molecules reaches to the SiC surface. Therefore, the H$_2$O partial pressure at the SiC surface is much lower than the partial pressure in the bulk gas. Oxidation is controlled by the transport rate of H$_2$O toward the SiC surface [1].

Based on Barat' oxidation model of SiC considering the transport rate of O$_2$ [2], H$_2$O partial pressure for the active/passive oxidation transition can be expressed by

$$P_{H_2O}^{transe} = 2\left(\frac{D_{SiO}}{D_{H_2O}}\right)^{3/8}\left(\frac{D_{CO}}{D_{H_2O}}\right)^{1/8} K_1^{3/4} K_2^{-1/2} \quad (3)$$

Diffusion coefficients, D$_{SiO}$ and D$_{CO}$, are 6.5 and 9.3 cm^2/s respectively which was approximated by Champman-Enskog equation [3]. D$_{H2O}$ was simply assumed to be 10 cm^2/s. Thermodynamic correlation

for the active/passive oxidation transition of SiC is shown in Fig. 4. H$_2$O partial pressure of SiC in the impurity-controlled helium is located on the boundary region of the active/passive oxidation transition.
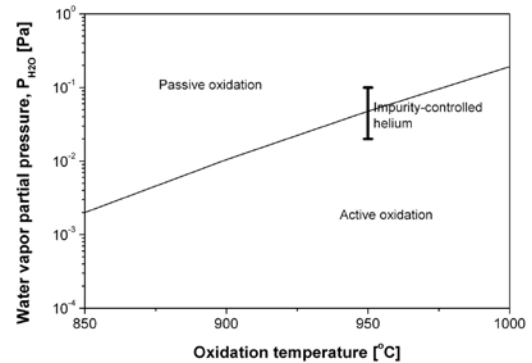

Fig. 4. Water vapor partial pressure for active/passive oxidation transition of SiC.

In summary, SiO$_2$ was formed by the passive oxidation at the initial stage of oxidation because the rapid H$_2$O transport through a thin boundary layer between SiC surface and the bulk gas. H$_2$O gradually consumed and reaches to steady state. After then, the oxidation rate is significantly reduced which results in the constant XPS peak intensity after 50 hours.

4. Conclusions

The oxidation behavior of CVD β-SiC was investigated at 950°C in the impurity-controlled helium environment that contained H$_2$, H$_2$O, CO, and CH$_4$. XPS and AFM analysis results indicated that a very small amount of SiO$_2$ was formed by the reaction of SiC with H$_2$O at the initial stage of oxidation when H$_2$O partial pressure in the CVD β-SiC surface placed on the passive oxidation region. As the oxidation progressed, H$_2$O consumed and its partial pressure in the surface decreased to the active/passive oxidation transition region. Therefore, more oxidation did not observable up to 250 hours of exposure at the steady state.

Acknowledgement

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