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Relationship Between Microstructure and Oxidation Resistivity of SiC Coating Layer

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Abstract: In a Very High Temperature Reactor (VHTR), the components of the next generational hydrogen production reactor, core and reflector are surrounded by graphite supports. Graphite materials, despite their excellent physical properties, oxidize easily above 500°C. For this reason, to prevent oxidation, a silicon carbide coating is often used. Among the physical vapor deposition methods, electron-beam coating easily develops cracks on the coating layer by thermal shock after application, forming a graphite oxidation path. In order to heal the cracks caused by thermal shock in the coating layer, this study adjusted the hydrogen ratio via. the Chemical Vapor Deposition (CVD) method and caused vapor distribution of SiC on specimens with cracks to heal. With a higher hydrogen ratio, the H_2 dilution effect is intensified. This causes an enhancement in the crystallizability which changes the round-shaped microstructure into a faceted microstructure. Further, the higher the hydrogen ratio, the denser the microstructure becomes which causes higher oxidation resistivity as well. Consequently, this study found that the anti-oxidation effect was sharply increased when the healing of coating layer cracks occurred at the hydrogen ratio of 200 via. the CVD method.

Key words: Chemical Vapor Deposition (CVD), Silicon Carbide (SiC), oxidation resistance, crack healing, hydrogen, Suwon

INTRODUCTION

The Very High Temperature Reactor (VHTR) is a next generation hydrogen reactor receiving attention as a future environmentally-friendly energy source. The VHTR can produce hydrogen and electricity that can be applied to a wide range of areas (Hwang *et al.*, 2011). The core and reflector components of a VHTR used at high temperature are supported by different kinds of graphite materials (Kim and Kim, 2008). Graphite has the properties of high thermal conductivity, with a low thermal expansion coefficient and low elasticity modulus. Thus, graphite is broadly utilized as a high-temperature structural material (Boo *et al.*, 2000). However, graphite begins to oxidize at 500°C and at the temperature of 900°C, it oxidizes more rapidly (Kim *et al.*, 1995). Oxidization, originating in graphite defects and pores, undermines the physical characteristics of the graphite to a great extent, reducing VHTR core lifespan and safety. Study of this phenomenon is necessary to prevent such a situation (Kim *et al.*, 2015).

In general, SiC is widely utilized as a coating material for its excellent oxidation resistivity and good compatibility with graphite materials (Qiang *et al.*, 2016). Moreover, SiC is a coating material that protects graphite when used in high temperature, corrosive, or abrasive conditions (Kim *et al.*, 2011a, b). Physically deposited SiC, however, is prone to cracks from thermal shock. These cracks open a path for oxygen to reach the graphite. Therefore, once the SiC coating layer is cracked, graphite oxidizes easily. For this reason, it is necessary to develop a technology capable of healing the cracks in a physically deposited SiC coating layer.

Chemical Vapor Deposition (CVD) is a deposition technology that produces the highest-quality SiC (Myers *et al.*, 2005). This technology provides nanoscale deposition which is smaller than the microscale deposition of Physical Vapor Transport (PVT), producing a more even structure (Saketi and Olsson, 2017). The present study healed cracks in physically deposited SiC, in different hydrogen ratios based on the CVD and evaluated the healed SiC deposited microstructure as well as oxidation resistivity, expressed in reaction velocity.

MATERIALS AND METHODS

Experimental procedures: CH_4 was used as the C source gas and liquefied $SiCl_4$ was used as the Si source gas. $SiCl_4$ was used after bubbling with H_2, the carrier gas. H_2

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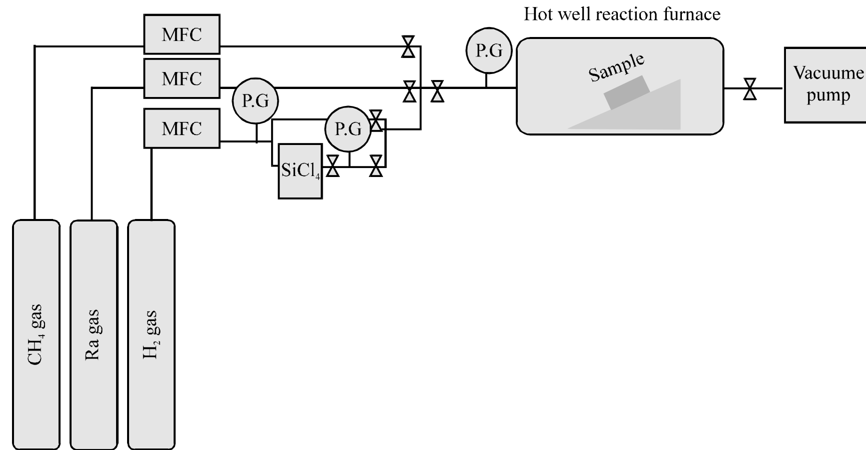

Fig. 1: Schematic of the CVD system used for crack healing

and Ar were used as ambient gases. The purging gas was Ar. A Mass Flow Controller (MFC) was used to adjust gas flow with high precision.

The $SiCl_4$ gas supply flow is calculated using the carrier gas flow, $SiCl_4$ vapor pressure and $SiCl_4$ temperature. Equilibrium state gas melting is determined via. Eq. 1 (Jung *et al*., 1997):

$$F_r = \frac{F_c P_r}{P_o - P_r} \quad (1)$$

F_r, P_0, F_c and P_r represent the flow and exhaust pressure of the reactant, carrier gas flow and vapor pressure of the reactant, respectively.

The CVD device used in this experiment is a hot-wall-type and the reaction tube is made of alumina (Φ = 70 mm×L = 1000 mm). Figure 1 shows the structure of the CVD device used for crack healing. In this experiment, the initial vacuum in the reaction tube was maintained at $<10^{-3}$ Torr and the purging gas, Ar was added by 50 sccm to increase the temperature until the deposition temperature was achieved. When the deposition temperature of 1300°C was reached, hydrogen gas was injected for 10 min to remove the remaining hydrocarbon impurities. Next, $SiCl_4$ was bubbled with the carrier gas and when all relevant pressures and flow were stabilized, the reaction gas was added to begin deposition. For homogeneous crack healing, the reaction gas methane ratio (CH_4/CH_4+SiCl_4) was fixed to 0.6, then, the hydrogen ratio (H_2/CH_4+SiCl_4) was changed while implementing the crack healing SiC coating for 60 min (Kim *et al*., 1995). In sample 1 with a hydrogen ratio of 100 and sample 2 with a hydrogen ratio of 200, CVD crack healing status was compared by observing their oxidization characteristics.

The first SiC deposition layer was deposited using cylindrical-shape graphite in the Electron beam (E-beam) evaporation coating method, a common PVD method.

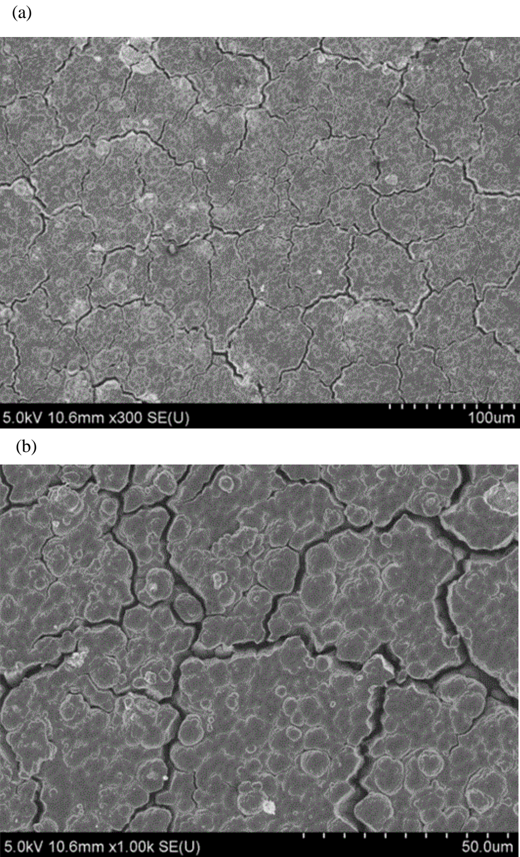

Fig. 2: Micrographs of SiC crack: a) ×300 and b) ×1000 K

Then, the SiC, treated using the E-beam coating method in diverse conditions was processed by thermally cycling with temperatures as high as 500-1000°C for thermal stability assessment. In this process, though the SiC is not exfoliated, it is cracked because of thermal shock (Fig. 2). These cracks become the path of graphite

oxidization, weakening the physical characteristics of the graphite. To prevent this, crack healing was performed using CVD.

In the oxidization test, the specimen with CVD healing of SiC was fixed in an oxygen environment with temperature rising from 600-900°C. Then, its weight change was measured to identify the degree of oxidization. To measure microstructure, Scanning Electron Microscopy (SEM, S-4800, HITACHI, Japan) was used for measurement. The acceleration voltage to obtain an image was analyzed using 5 kV. The oxidization velocity at the oxidization temperature of 900°C on the weight reduction curve was calculated using the Arrehenius plot of Eq. 2 (Eiichi, 1996):

$$k = \frac{\Delta W}{W_0 . \Delta t} = A\exp\left(\frac{-\Delta E}{R.T}\right) \quad (2)$$

Where:

W_0 = The pre-oxidization specimen weight (mg)
ΔE = Activation Energy (kg/moL)
ΔW = Weight decrease by oxidization
Δt = Minutes (mg)
R = Gas constant (8.314 kJ/moL.K)
K = Reaction velocity (mg/mg.min)
A = Proportionality constant
T = Temperature (K)

RESULTS AND DISCUSSION

Morphologies of SiC coating layers with respect to H_2 ratio: Figure 3 shows the comparison of microstructures under the conditions of hydrogen ratios of 100 and 200. It was found that the microstructure changed from a rounded structure to faceted structure of crystal grains with an increase in the hydrogen ratio. Lee *et al*. (2001) reported that the rounded microstructure was observed mainly at 1200°C or lower while the faceted structure occurred at 1250°C or higher, under rising pressure. Reportedly, this is because with an increase in deposition temperature, mass transfer works as a dominant reaction mechanism. But in the present study, sufficient reaction took place to form a faceted microstructure because a very high concentration of reaction gases existed at both hydrogen ratios of 100 and 200 (Kim *et al*., 1995). Further, the larger the amount of H_2, the more pronounced the H_2 dilution effect becomes which causes more crystallizability of amorphous SiC. Another possible reason for this effect could be the formation of polycrystalline SiC on the SiC crack surface (Seo *et al*., 2001). In this manner, the most appropriate hydrogen ratio was deemed between 100 and 200 to minimize the loss of injected gas while controlling silicon

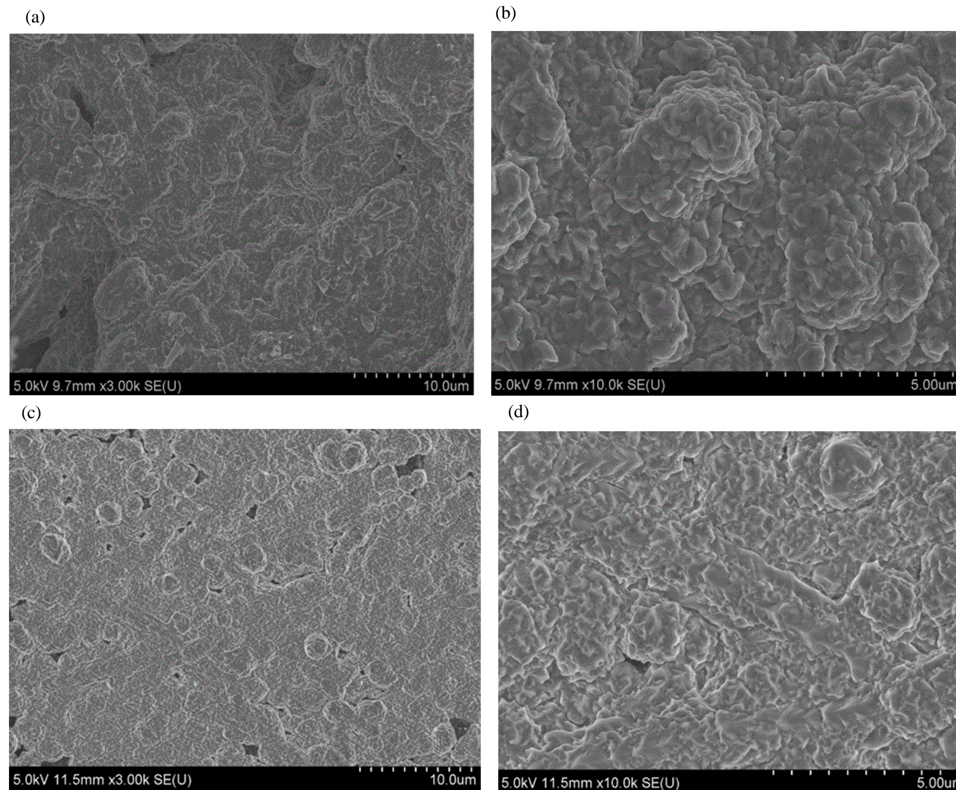

Fig. 3: Micrographs of SiC: a)×3.00 K; (b) ×10.0 K at H_2 ratio 100; c) ×3.00 K and d) ×10.0 K at H_2 ratio 200

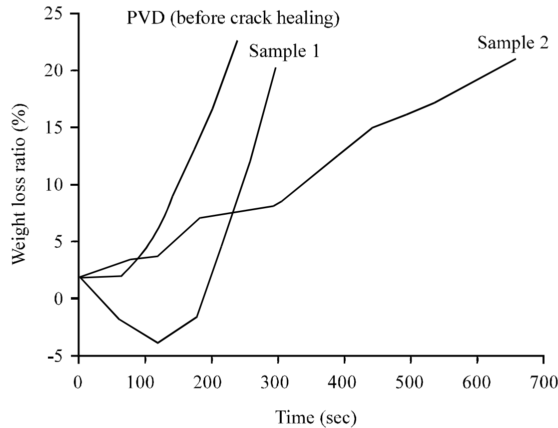

Fig. 4: Weight loss ratio vs. time at 900°C

eduction (Kim *et al*., 2011a, b). Thus, crack healing was performed at the hydrogen ratio of 100 and 200. Next, the two specimen oxidization status was compared in order to identify crack healing effectiveness.

Oxidation resistance with respect to H_2 ratio: To investigate the oxidation resistivity of crack healed SiC, the oxidation resistivity differences were compared between hydrogen ratios of 100 and 200. Figure 4 shows the weight changes in the two specimens at 900°C. Sample 1 received the crack healing process at the hydrogen ratio of 100 and sample 2, at 200. As shown in Fig. 4, sample 2 showed a far greater oxidization resistivity.

It is deemed this is because the higher the hydrogen ratio, the more faceted the structure becomes, thus, making a denser crack healing layer microstructure, resulting in stronger oxidation resistivity.

The faceted structure appearing at the high hydrogen ratio is the kind of microstructure often observed at a 1300°C deposition temperature. Air diffusion at this temperature takes place through Fick's diffusion device. At a deposition temperature of 1100°C, air is diffused mainly through the Knudsen diffusion device.

Compared to the Knudsen diffusion, Fick's diffusion was reported to have a lower oxidation resistivity by Kim (2007). In this present study, however, the faceted structure at 1300°C was found to have a higher oxidation resistivity, although, the rounded structure appearing at 1100°C was observed at a lower hydrogen ratio. Such a contradictory result is deemed to occur because the higher the hydrogen ratio, the more reaction gas is available to create more reactions and densify the microstructure.

Table 1 shows the reaction velocity measured based on the Arrhenius plot. The reaction velocity was found to show the same trend as the weight reduction graph. Sample 2 showed the slowest reaction velocity and oxidization velocity, demonstrating its excellent oxidation resistivity. Further, the physically deposited PVT (pre-crack healing specimen) showed the fastest reaction velocity (Kim and Chae, 2017).

Table 1: Arrhenius plot for oxidation rate at 900°C under air conditions

Sample	lnK(mg/mg.sec)
PVD (before crack healing)	-13.564
Sample 1	-13.639
Sample 2	-15.029

This finding is deemed to occur because when deposited physically, defects such as micro-pipes or dislocations could be mixed with the SiC deposition and crack the coating layers due to thermal shock (Elhaddad, 2010).

CONCLUSION

This study employed CVD to heal the cracks in a SiC coating layer and identified the oxidation resistivity of healed SiC to compare the oxidization resistivity degrees, according to different hydrogen ratios. As a result, the microstructure was found to change from a rounded structure to faceted structure as the hydrogen ratio rose. Likewise, for the oxidation resistivity, the higher the hydrogen ratio, the lower the oxygen reaction velocity and the slower weight change.

The findings are deemed to occur because the faceted microstructure is denser than the rounded microstructure and has a stronger oxidation resistivity. Thus, at the hydrogen ratio of 200, the surface could be denser as a result of the high reaction-gas concentration. The CVD-coated specimen at the hydrogen ratio of 200 was found to have the strongest oxidation resistivity in this study. Therefore, it is desired to employ the CVD crack healing method at a high hydrogen ratio for crack healing of the graphite coating layer used in the VHTR. In this manner, SiC oxidization resistivity could be effectively improved.

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