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DEVELOPMENT OF SUPERIOR THERMAL PROTECTIVE COATING ON CARBON COMPOSITES

A superior SiC based thermal protection coating process for carbon composite, which can be especially effective in a hot oxidizing atmosphere, was established in this study. A multi-coating process based on a combination of Chemical Vapor Reaction (CVR) and Chemical Vapor Deposition (CVD) was developed. Various protective coating layers on carbon composite were tested in hot oxidizing surroundings and the test results verified that the thermal ablation rate could be dramatically reduced down to 3.8% when the protective multi-coating was applied. The thermal protection mechanism of the coating layers was also investigated.

Keywords: Composite, Silicon carbide, CVR, CVD

1. Introduction

Carbon composites are well known as superior heat-resisting materials in various applications including braking systems, nozzles and jet engines, as well as civil purposes, due to their outstanding heat-resisting characteristics, including thermal shock resistance and sustainable high specific strength at high temperature [1,2]. However, the carbon based composites have limited application in oxidative environments because of the relatively low oxidation temperature of carbon species [2]. In this regard, enormous efforts have been conducted to strengthen the anti-oxidation characteristics of carbon composites [3-8]. Among the various approaches, coating the carbon composites with anti-oxidation ultra-high temperature ceramics such as Silicon Carbide (SiC) can be a good candidate considering its desirable anti-oxidation characteristics, low heat-expansion coefficient, affordable process cost and so on.

Various coating methodologies such as pack cementation [4,5], plasma spraying [4,6], Chemical Vapor Deposition (CVD) [7], slurry sintering [8] and Chemical Vapor Reaction (CVR) [4] have been widely used to form a SiC coating layer on various substrates.

Here we report a new facile coating process based on the combination of CVR and CVD processes for the formation of sound SiC coating layer with enhanced heat-resistant performance of carbon composite. Firstly, the optimum coating processes were developed respectively for CVR and CVD. Then, those two coating processes were combined to obtain hybrid coating(CVR/CVD) of SiC layers. Finally, the thermal protection capabilities of the coating layers obtained *via* the CVR, CVD and CVR/CVD processes were verified by oxy-kerosene torch test and the thermal protection mechanism of the coating layers was also investigated.

2. Experimental

2.1. Fabrication of specimens

The carbon composite was fabricated using carbon fiber, Hyosung H2550 with needle punch process and a consequent densification/carbonization process using coal tar pitch as the matrix precursor. Then, the carbon composites were machined to coin size samples, Φ30 mm × 5 mm, to characterize the properties of the composites.

On the coin size samples, SiC coating was performed using the CVD or/and CVR coating methods. To evaluate the characteristics of the coating layers in relation to the number of CVD cycles, and the effect of CVR as an inter-layer between the carbon composite and CVD layer, four kinds of samples were fabricated. The four samples were designated R, D1, D2 and RD1 according to the coating methods and cycles (Table 1).

R, D1 and D2 respectively indicates CVR one cycle (1cy.), CVD one cycle (1cy.) and CVD two cycle (2cy.) were

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TABLE 1

Sample designations according to coating method and CVD coating cycles

Sample name	Coating method and condition
R	CVR
D1	CVD 1cy.
D2	CVD 2cy.
RD1	CVR + CVD 1cy.

performed. RD1 means the CVR process was performed on the coin sample first, and one cycle (1cy.) of the CVD process was applied additionally.

To prepare the SiC CVD coating, the low-pressure chemical vapor deposition (LP-CVD) method was applied to the coin size carbon composites with Methyltrichlorosilane (MTS) gas and H_2 gas at 1250°C. The MTS flow rate was 6.7 cc/min and the concentration ratio of MTS gas in H_2 gas was 7.5%. The reaction time was 24 hours for one cycle.

The SiC CVR layer was prepared with SiO_2 powders. In a graphite reactor, the carbon composites and SiO_2 powders were heated up to 2200°C with nitrogen gas for 120 min. SiO_2 was transformed to SiO vapor which could react with the carbon composites as shown below.

$$SiO_2(s) + C(s) \rightarrow SiO(v) + CO(v) \tag{1}$$

$$SiO(v) + 2C(s) \rightarrow SiC(s) + CO(v) \tag{2}$$

After the reaction, the furnace was cooled down to room temperature. The SiC and SiO_2 particles formed were removed *via* sandblasting.

2.2. Characterization of specimens

The morphologies of the SiC coated samples were analyzed using Scanning Electron Microscopy (SEM). To verify the phase composition of the SiC crystals, an X-ray Diffraction (XRD, Bruker D8 advances) experiment were conducted.

The ablation tests were carried out in a blowing oxy-kerosene torch environment using a HVOF (high velocity oxygen fuel) system. The HVOF system generates a high temperature torch by combusting an oxygen-kerosene fuel mixture. The oxygen flow rate was 21,500 SCFH and the kerosene flow rate was 2 GPH. The coated coin shape samples were exposed to the flame parallel to the axial orientation. The distance between the sample and nozzle tip was 88 mm and the temperature at this point is around 1700°C, measured by pyrometer. The test was performed until the flame had penetrated the samples, whose longer penetration time means better ablation resistance.

The roughness of surface was measured using a "SJ-210", Portable Surface Roughness Tester, made by Mitutoyo in Japan.

3. Results and discussion

Fig. 1 shows SEM images of the cross-sectional morphologies of the SiC coated samples, R, D1, D2, and RD1, which were prepared using CVR and CVD processes. The thickness of the coating on R is 10-30 μm, D1 is 30-40 μm, D2 is 90-110 μm, and RD1 is 50-70 μm.

For D1 and D2, deposition by the MTS gas was more dominant than penetration in the CVD process, and the thickness

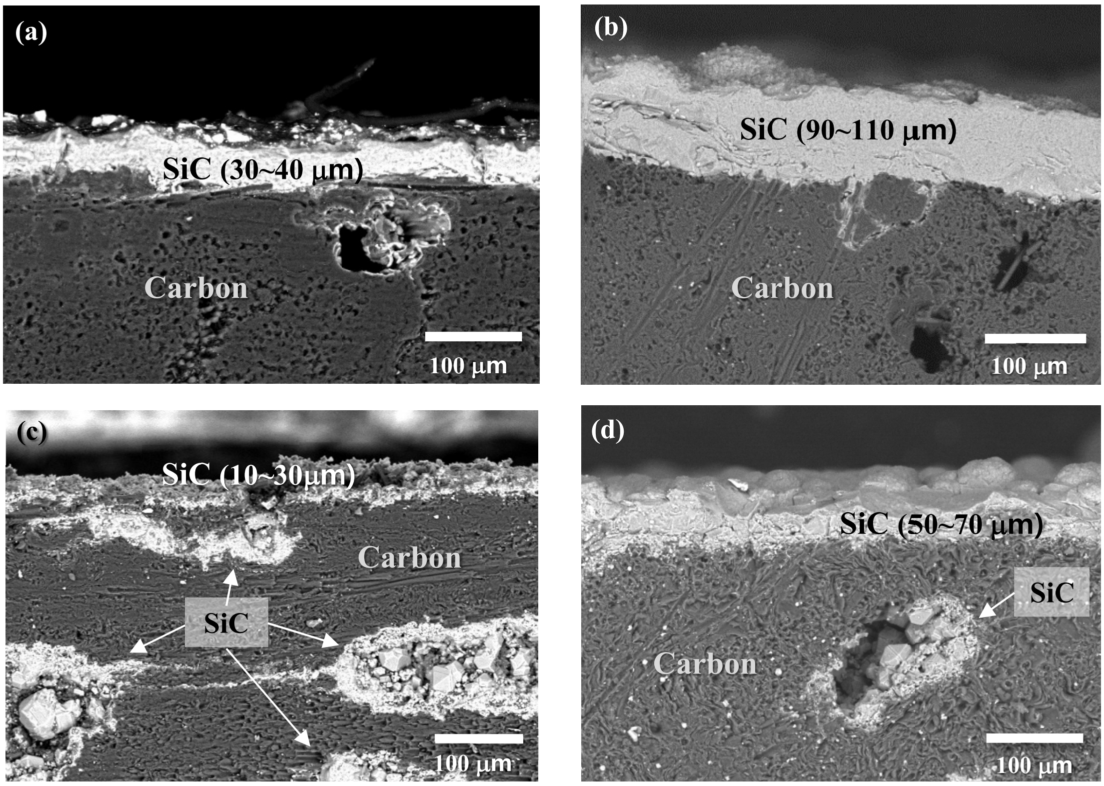

Fig. 1. Morphologies of the cross-sectioned samples (a) D1, (b) D2, (c) R and (d) RD1

of the coating grew as deposition progressed. In this respect, the average thickness of the coating layer on D2 was 104 μm. This is more than double the coating thickness of D1, which was 35.5 μm.

In Fig. 1(c), a considerable part of the carbon composite of R sample, especially around the pores, is transformed to the SiC phase. The average coating layer on the carbon composite was 25 μm, and it is relatively low compared with D1. The CVR process was conducted at high temperature, 2200°C, and the gas source was able to easily penetrate into the pores of sample R.

In Fig. 1(d), RD1 also contains transformed SiC phase in the substrate as well as R. By comparing SEM images of cross sectional samples of R and RD1, it was confirmed that there was no significant change in morphologies, including crystal size growth. The SiC phase in carbon composite substrate formed by the CVR coating was not changed after the CVD processing because the CVD reaction temperature was much lower. The average coating thickness of RD1 was 69 μm, relatively lower than that of D2.

Fig. 2 shows the XRD patterns of R, D1, D2 and RD1, the SiC coated samples fabricated using the CVR and CVD processes, respectively. As shown in Fig. 2, the surface of R contains a mixture of α-SiC and β-SiC phases, while D1 and D2 only contain β-SiC. The XRD result for RD1 shows a pattern similar to D1. This is a natural phenomenon, because the coating thickness of the SiC layer formed via CVD is 30~40 μm, and the detectable depth of XRD for this sample was under 30 μm. The CVR coating layer of RD1 is under the CVD layer, so the SiC phase of the α-SiC and β-SiC from CVR is not detectable.

The surface morphologies of R, D1, D2 and RD1 are shown in Fig. 3. In the SEM image with 500 μm scale, on the surface of the D1, D2 and RD1, fine and small SiC aggregation could be observed. It is expected that liquid droplets consisting of Si, C, Cl and H might be transformed to aggregated SiC due to supersaturation during the CVD process [7].

High magnification images (inset of Fig. 3) reveal that SiC crystals on the surface becomes much smaller and more homogeneous in D1, D2 and RD1 compared to R.

The ablation test results using the HVOF system are shown in Fig. 4 and summarized in Table 2. The average penetration time of the carbon composite was about 7 seconds. The ablation rate of the coated samples, D1 was 0.17 mm/s, and R was 0.15 mm/s, respectively.

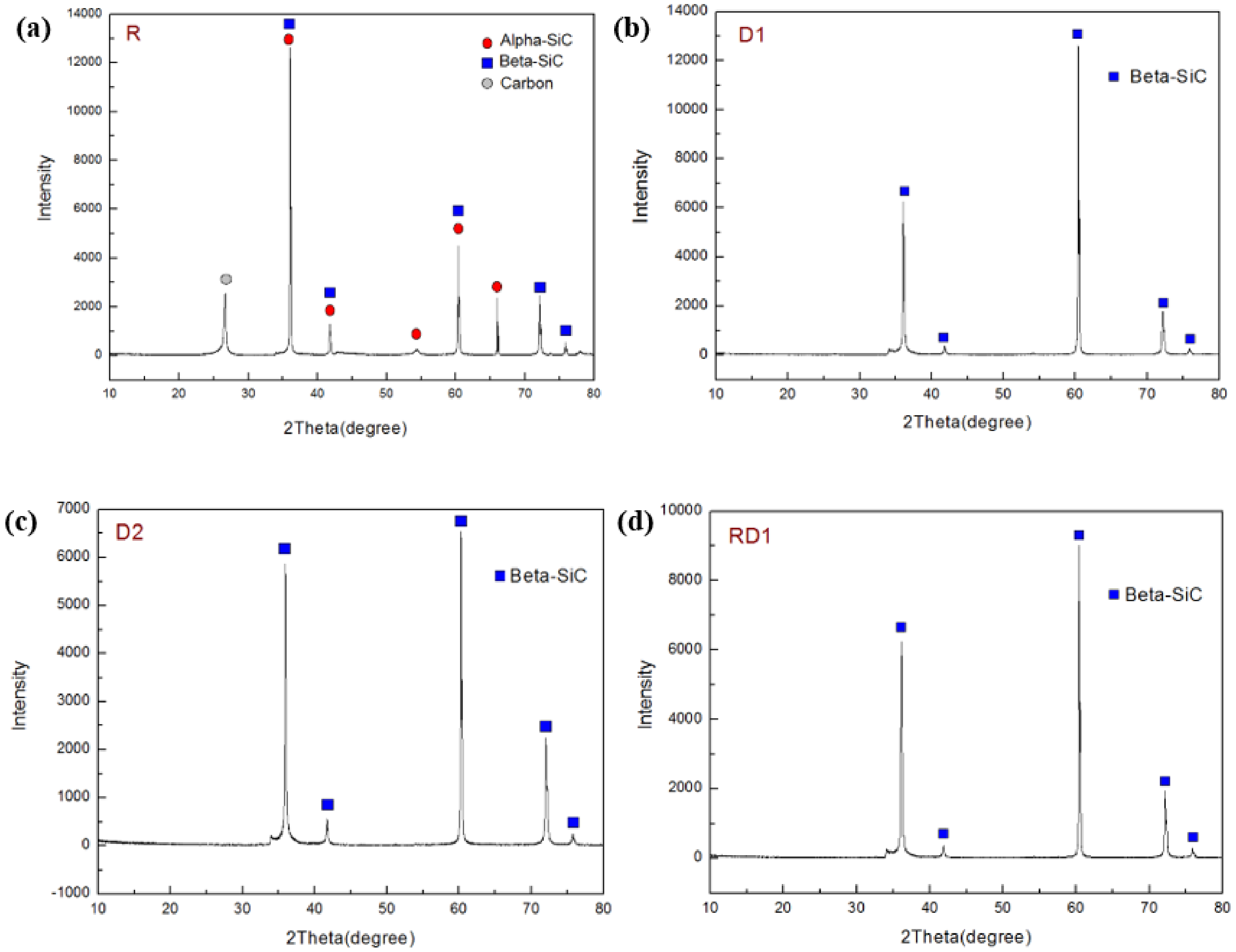

Fig. 2. XRD spectra of the samples: (a) R, (b) D1, (c) D2 and (d) RD1

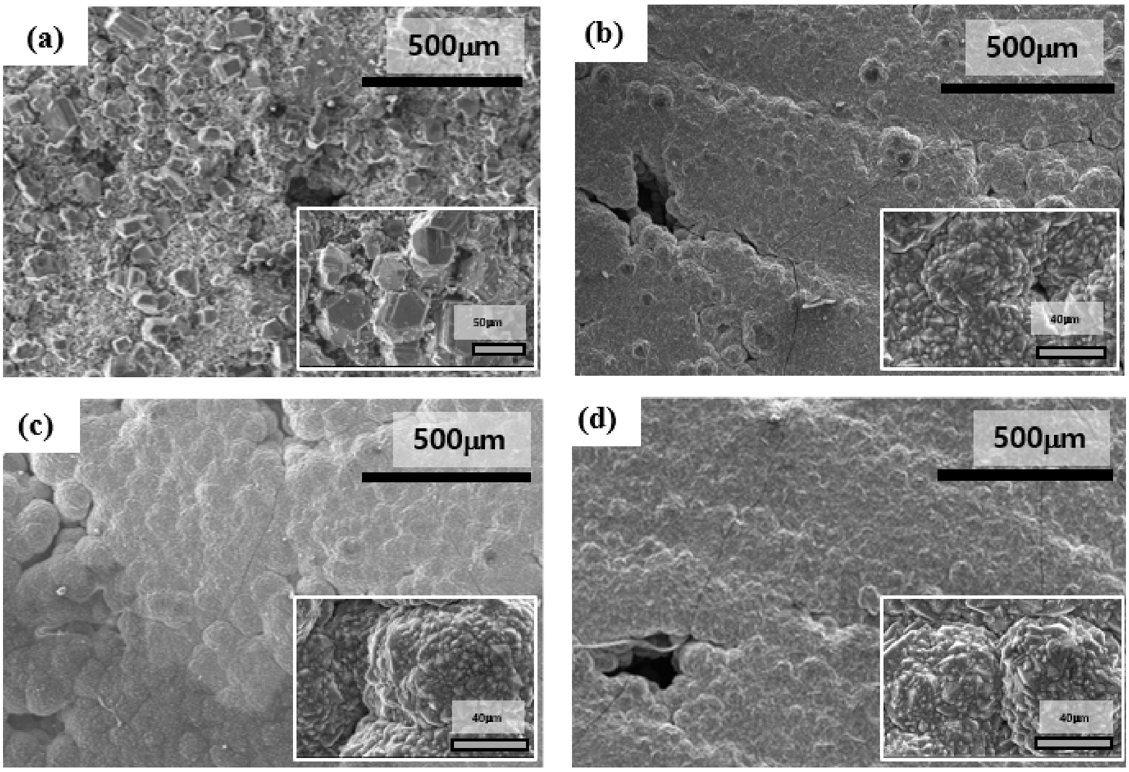

Fig. 3. Surface SEM images of the coated samples: (a) R, (b) D1, (c) D2 and (d) RD1

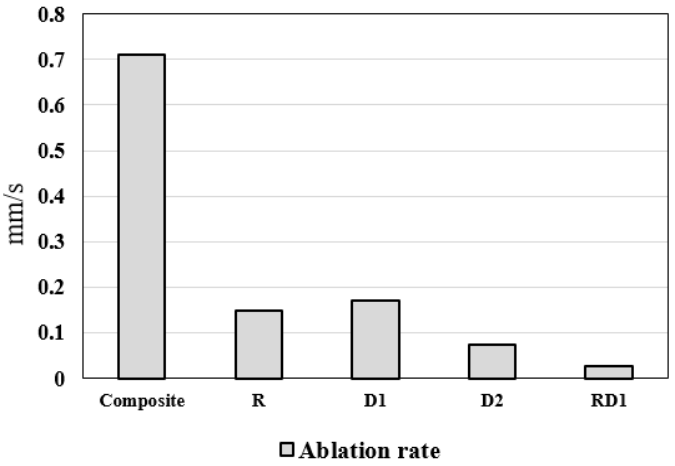

Fig. 4. The ablation rate of the carbon composite and coated samples

TABLE 2

Average thickness and ablation properties of carbon composite and coated samples

Sample name	Average thickness of coating layer (μm)	Penetration time (s)	Average ablation rate (mm/s)
Composite	—	7±1	0.71
D1	35.5	29±13	0.17
R	25	32±3	0.15
D2	104	66±21	0.075
RD1	69	188±38	0.027

These rates are just about 25% of those of the carbon composites, which proves that the CVR and CVD coatings plays an important role as a heat-protection coating of the carbon composite at high temperature in oxidizing surroundings. For D1 and D2 samples, homogeneous dense coating layers could protect the carbon composite against the high velocity flame.

During the test of R, flames could penetrate into the SiC phase of the carbon composite substrate, and the flame penetration could be effectively deterred. As listed in Table 2, RD1 showed the lowest ablation rate of 0.027 mm/s, which is just 3.8% of the bare carbon composite. This result was even superior to D2, and applying the interlayer via CVR applying the inter-layer between the carbon composite and the CVD coating layer via CVR was confirmed to have a significant effect on the thermal protection of the carbon composites.

It is note-worthy that the CVR coating on composite substrate increases the surface roughness value (Ra) from 11.9 (Composite) to 18.5 (R) as listed in Table 3. One of the attractive features of applying CVR as an inter-layer between composite substrate and CVD coating layer is the increased surface roughness of R. Although the highly rough surface can be a weak point in case of outer-most coating layer, we expect that the high roughness and the consequent large surface area of R can

TABLE 3

The average roughness values of carbon composite and coated samples

Sample name	Roughness value (Ra)
Composite	11.9
D1	8.5
R	18.5

play an excellent role as an inter-layer allowing more chance of adhesion with following outer coating layer. In addition, stronger bonding between this inter-layer and the following outer layer can be expected due to the elemental similarity (SiC on SiC; RD1 sample), compared to the direct coating of on bare carbon composites (SiC on C; D1 or D2 samples). The outstanding penetration time delay that we described earlier (Table 2) can also be interpreted from these perspectives.

4. Conclusion

In this report, we propose a strategy for improving heat-resistant characteristics of silicon carbide based coating *via* simple combination of well-known coating methods, CVD and CVR. Oxy-kerosene torch test revealed that our approach based on the combination of CVD and CVR can lead outstanding penetration time delay compared to the other coated- or uncoated cases. Further investigation based on analysis by surface/cross section SEM and XRD provided physicochemical properties and overall understanding of the beneficial role of inter-layer in our approach. This results shows great potential for use in various carbon based materials that requires advanced heat-protective and anti-oxidative characteristics in diverse applications.

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