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Effect of coating defects on oxidation behavior of three dimensional C/SiC composites from room temperature to 1500°C

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Oxidation tests of a three-dimensional C/SiC composites with different coatings were conducted in dry air and the effect of defects in the coatings on the oxidation behavior were investigated. There existed two kinds of preparation defects in the CVD SiC coating, including the supporting defects and the machining defects. The former were produced by supporting of the specimens and the later were produced from the matrix pores formed between the fiber bundles after machining. There existed two kinds of deposition defects in the multi-layer CVD SiC coating, including the plane-defects and the net-defects. The former were formed between the layers and the later were produced at the boundaries between the particles. Increasing the coating thickness can seal the machining defects, but it can not seal the supporting defects. Multi-deposition can not completely seal the preparation defects although it decreased remarkably the weight loss. The Si-Zr outer layer can seal completely defects in the multi-layer, but it increases the weight loss at low temperature, and furthermore has a low resistance to oxygen diffusion. The borosilicate glass can seal the coating cracks, but it nearly loses all ability of sealing defects at high temperature. The preparation defects can be completely sealed if there exist no plane-defects in the multi-layer coating. Increasing the deposition temperature and decreasing the deposition pressure will be favorable to removing the plane-defects.

1. Introduction

Chemical vapor infiltration (CVI) has been widely used for preparing three-dimensional carbon fiber reinforced silicon carbide composite (3D-C/SiC) [1–4]. In the last stage of CVI processes, a SiC coating will be formed on the composite due to surface deposition. Theoretically, the CVD SiC is the most promising coating for the C/SiC composite. Firstly, preparation of the composite and the coating can be conducted at the same time, and then the special equipment and technology for preparing the coating are not needed. Secondly, a gradient SiC layer can be formed between the coating and the composite, then the coating has thinner cracks owning to the lower mismatch with the composite. Lastly and most importantly, the formation of silica on the coating surface is favorable to the oxidation protection of the C/SiC composite because the silica has a small diffusivity of oxygen and a certain ability to seal the coating cracks [5]. The oxidation of CVD SiC is passive up to 1700˚C. If there are no defects, oxidation protection of SiC coatings for C/C should be long-time. However, it has been found that the oxidation protection time of the coating is much shorter than that expected after the coating cracks are sealed with increasing temperature. This can only be considered to be caused by defects in the coating. Because carbon fibers are employed, the C/SiC composite is very sensitive to the defects in the coating.

Some investigations have been conducted on the formation mechanism of defects in the CVD SiC film [6, 7]. The kinds and the formation mechanisms of defects in the CVD sic coating, especially in multi-layer coating, on composites have not been studied. In the current article, CVD SiC coatings with different layers were prepared on the C/SiC composite and sealed by a Si-Zr outer layer and a borosilicate glass sealent. Oxidation tests of a three dimensional C/SiC composites with different coatings were conducted in dry air and the effect of defects in the coatings on the oxidation behavior were investigated.

2. Experimental procedure

2.1. Fabrication of the specimens

A three-dimensional C/SiC composite was prepared by low-pressure chemical vapor deposition method (LPCVI). The preforms were deposited with pyrolysis carbon (PyC) and SiC using butane and methyltrichlorosilane (MTS). The deposition conditions of PyC interlayer were as follow: temperature 960°C, pressure 5 KPa, time 20 hours, Ar flow 200 ml $\cdot$ min^{-1}, butane flow 15 ml $\cdot$ min^{-1}. The deposition conditions of

SiC matrix were as follow: temperature 1000°C, pressure 5 KPa, time 120 hours, H_2 flow 350 ml $\cdot$ min^{-1}, Ar flow 350 ml $\cdot$ min^{-1}, and the molar ratio of H_2 and MTS was 10. Substrates with a size of 3 mm × 5 mm × 40 mm were machined from the fabricated composite with a size of 4 mm × 6 mm × 150 mm. Different coatings were prepared on the substrates. The one-layer SiC coating with a thickness of about 20 μm was prepared by deposition for 20 hours. The two-layer SiC coating with a thickness of about 40 μm was prepared by deposition for 40 hours. The three-layer SiC coating with a thickness of about 60 μm was prepared by deposition for 60 hours. The SiC/Si-Zr coating consisted of a SiC inner layer and a Si-Zr outer layer. The former with a thickness of about 20 μm was prepared by deposition for 20 hours, and the latter with a thickness of about 150 μm was prepared by liquid-reaction method at 1500°C for 30 minutes. The SiC/glass coating consisted of a SiC layer with a thickness of about 20 μm and a borosilicate glass selant. The glass consisted of 55–60%mol SiO_2 and 40–45%mol B_2O_3. The coated substrates were infiltrated by SiO_2 and B_2O_3 separately at room temperature, and then the glass was formed after sintering for one hour at 1000°C in a vacuum furnace.

2.2. Oxidation tests

Oxidation tests of all the specimens were conducted in dry air at different temperatures from 400°C to 1500°C. The specimens were separately weighted after oxidation of 2 hours, 5 hours and 10 hours.

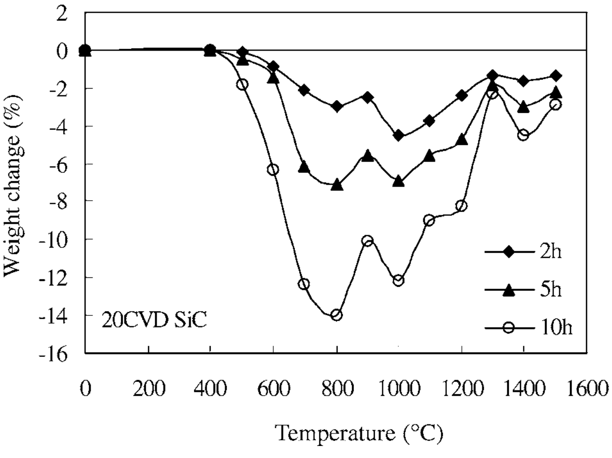
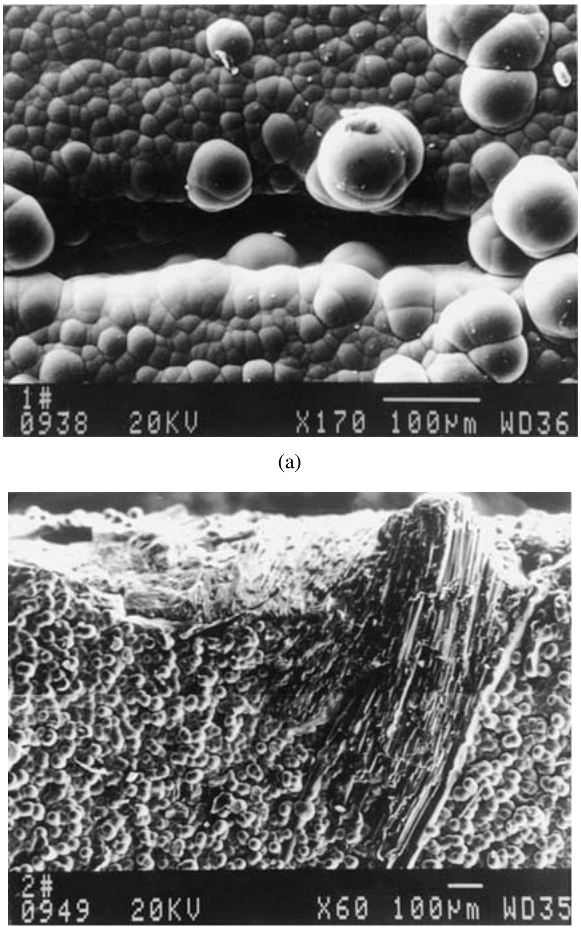


Figure 1 Relations of weight loss to temperature of the C/SiC composite with a one-layer CVD SiC coating after oxidation for different time.



(a)

(b)

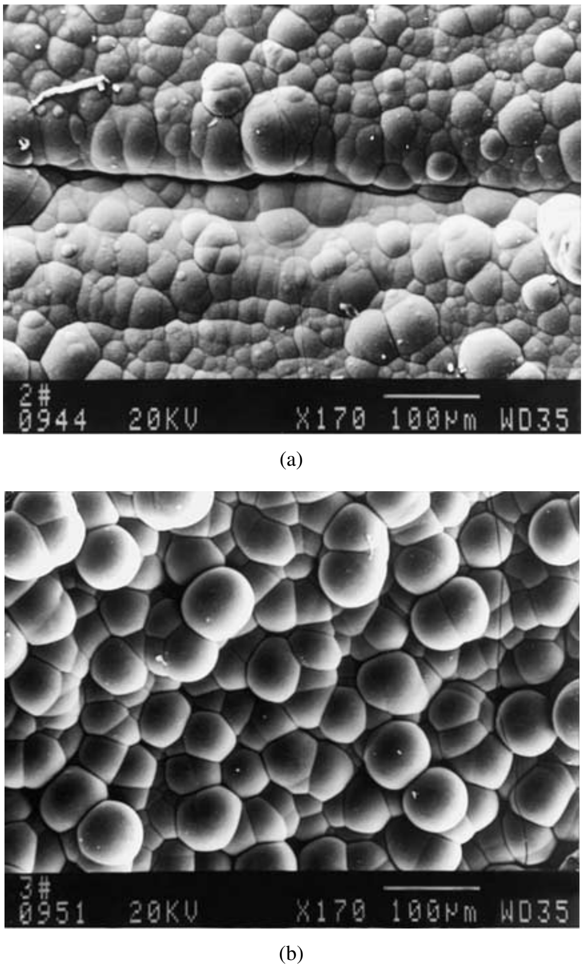
Figure 2 Two kinds of preparation defects in the SiC coating of a SiC composite (a) supporting defects, (b) machining defects.

3. Results and discussion

Fig. 1 is the relations of weight change to temperature of the SiC composite with the one-layer SiC coating after oxidation for different time. Below 800°C, the weight loss changed regularly and fit the Arrhenius' law. The activation energy for oxidation was calculated to be 24 kcal/mol after oxidation for 5 hours. Above 800°C, the composite always lost weight with increasing oxidation temperature, and the weight loss changed irregularly. The weight loss was considered to be produced by defects in the coating. Because of the mismatch between the coating and the substrates, cracks would be produced in the coating at some temperature below the deposition temperature. This temperature is called as the coating cracking temperature. The cracking temperature of the SiC coating is lower than 1000°C. If there were no defects in the coating, the composite would always gain weight because oxidation takes place only on the coating surface above the coating cracking temperature. Fig. 2 showed two kinds of preparation defects in the CVD SiC coating. No matter whether the substrates were suspended by carbon fibers or supported on a graphite retort, little SiC could be deposited at the suspension and support site, and more than one defects would be produced in the coating when the specimens were separated from the fibers or the retort. Being called as supporting defects, they were generally located at edges and corners of the specimens (Fig. 2a). The matrix pores formed between the fiber bundles were open on the surface of the composite after machined. The large pores could not be sealed by the SiC coating with a thickness of 20 μm, then they became the machining defects (Fig. 2b). Clearly, it was impossible to remove the preparation defects. Because the preparation defects became the channels of oxygen diffusion in oxidation process, the composite always lost weight above the coating cracking temperature. Below the coating cracking temperature, the composite always lost weight due to the coating cracks. Below 800°C, the preparation defects had no effect on the change of the weight loss with temperature although they became the channels of oxygen diffusion because the oxidation was controlled by the reaction of oxygen with carbon. As a result, the weight loss changed with temperature in the Arrhenius' law.

Obviously, increasing the coating thickness can seal the machining defects, but it can not seal the supporting defects. Increasing the coating layers can not only seal the supporting defects, but also seal the machining defects at the same time. The multi-layer coating can be prepared by multi-deposition. Therefore, multi-deposition is very necessary to increase the oxidation protection ability of the CVD SiC coating. In principle, the outer layer can seal the supporting defects in the inner layer of the two-layer coating provided that the substrates are supported at different points. It is reasonable to think that the supporting defects have not effect on oxidation of the composite with the two-layer coating. However, the two-layer coating did not completely seal the machining defects (Fig. 3a). After deposition for three times, the machining defects were completely sealed (Fig. 3b).

Fig. 4 is the relations of weight change to temperature of the C/SiC composite with the three-layer SiC coating after oxidation for different time. It can be seen that the composite with the three-layer coating lost weight over the full temperature range as that with the one-layer coating did. But the weight loss of the former fit the Arrhenius' law below 700°C, and was remarkably lower than the latter below 1400°C. From 700°C to 900°C, the weight loss of the former decreased regularly due to sealing of the coating crack with increasing temperature, and that of the latter changed irregularly because the preparation defects had a stronger effect than the coating cracks. All these indicated that multi-deposition decreased the effect of the preparation defects in the coating on oxidation behavior of the composite, but it did not seal them completely as expected. Undoubtedly, there were some channels between the preparation defects in the inner layer and those in the outer layer.



(a)

(b)

Figure 3 SEM micrographs of the machining defects in the SiC coating of (a) two-layer, (b) three-layer.

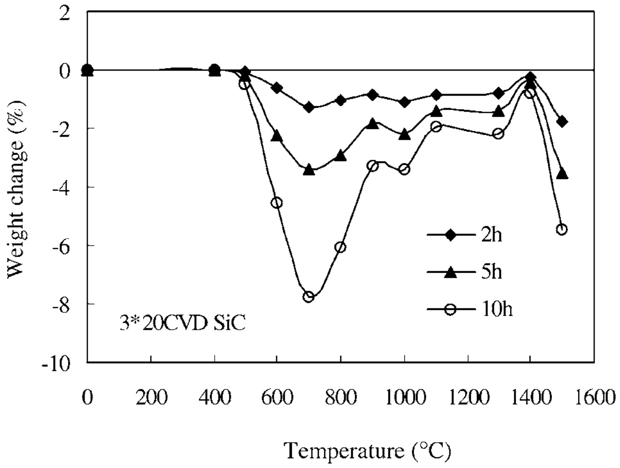
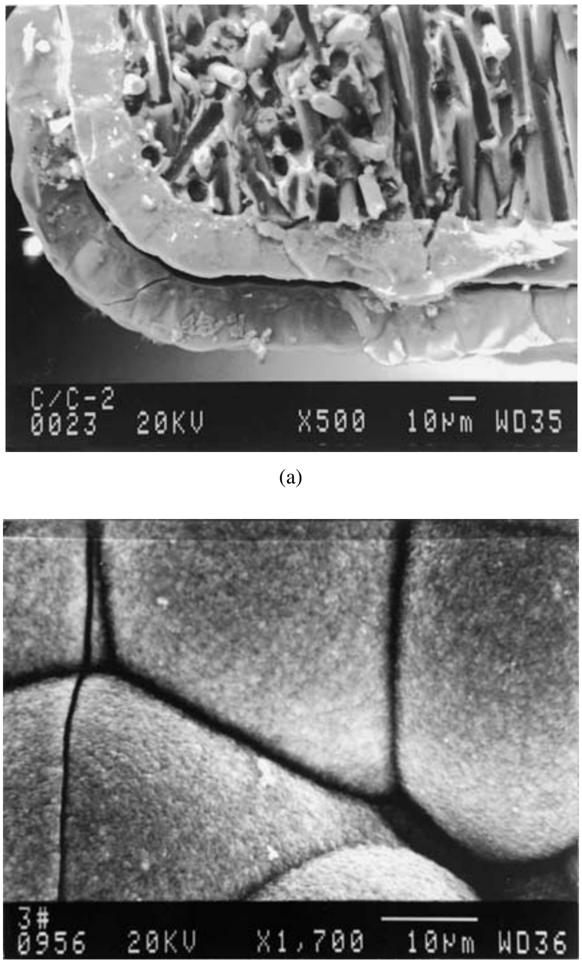


Figure 4 Relations of weight loss to temperature of the C/SiC composite with a CVD SiC coating after oxidation for different times.

It was not difficult to find that there existed another two kinds of defects in the multi-layer coating from its SEM micrographs (Fig. 5). There was always a large gap somewhere between the layers which were measured to be from 2 to 3 μm in width. When the gap connects the preparation defects in the inner layer with those in the outer layer, it will become the channels of oxygen diffusion. Because the gap is very large in two-dimension, it can be called as plane-defects (Fig. 5a). The SiC layer is composed of a large number of spherical particles with a cloud-cluster shape. It is easy to determine that each particle is an aggregate consisting of a large number of nanometer SiC crystallites [ ]. A larger number of gullies are formed at the boundaries between the particles due to the incomplete fusion of the particles. In other word, the layers are not completely dense although the particles are. Because the gullies are well distributed in the layer like a net as the boundaries does, they can be called as net-defects (Fig. 5b). It is impossible to avoid that the net-defects in the outer layer cross on those in inner layer. Even though there was not the gap between the layers, the net-defects would become the channels of oxygen diffusion. Because the formation of the plane-defects and the net-defects is related to the deposition process, these two kinds of defects can be called as deposition defects. The composite with the three-layer coating had a lower weight loss than that with the one-layer coating. Although the preparation defects were not sealed completely due to the deposition defects, the channels of oxygen diffusion were extended greatly by multi-deposition.



(a)

(b)

Figure 5 SEM micrographs of the two kinds of deposition defects in the multi-layer SiC coating (a) the plane-defects, (b) the net-defects.

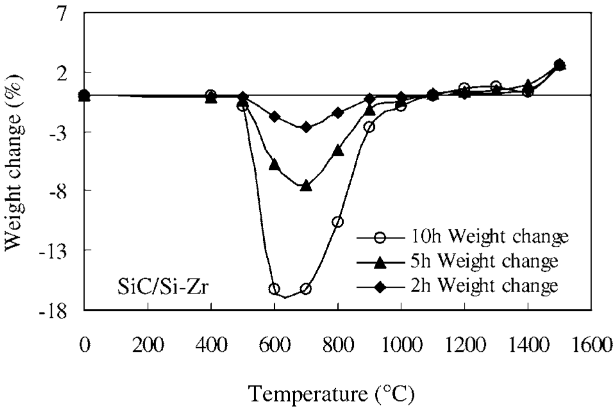


Figure 6 Relations of weight change to temperature of the C/SiC composite with a SiC/Si-Zr coating after oxidation for different times.

Fig. 6 is the relations of weight change to temperature of the SiC composite with the SiC/Si-Zr coating after oxidation for different time. Above 1050°C, the composite always gained weight, and the weight gain changed with temperature in an exponential law. This indicated that the weight gain was controlled only by the oxygen diffusion rate through the oxide film formed on the coating surface because it changed with temperature in an exponential law. Only there are no channels of oxygen diffusion in the coating, the oxidation can take place only on the coating surface. It can be concluded that the outer layer prepared by liquid-reaction method was completely dense. By spreading out of the outer layer, all the defects in the inner layer were sealed. From 400°C to 1050°C, the composite always lost weight due to the coating cracks. Comparing Fig. 6 with Fig. 4, it can be found that the weight loss of the composite with the SiC/Si-Zr coating is much higher than that of the composite with the three-layer SiC coating. Because no defects had effect on the weight loss, it was controlled by the reaction of carbon with oxygen and the oxygen diffusion through the cracks. The higher the temperature, the greater the effect of the reaction on the weight loss, but the smaller the effect of the diffusion. The lower the temperature, the smaller the effect of the reaction on the weight loss, but the greater the effect of the diffusion. As a result, the weight loss reached its maximum value at 700°C. The Si-Zr layer was prepared at much higher temperature and had a larger thermal expansion than the SiC layer, then the SiC/Si-Zr coating had a larger thermal mismatch with the substrates than the three-layer SiC coating. It can be concluded that the Si-Zr outer layer increased the width of the coating cracks although it sealed completely the defects in the SiC inner layer.

The defects mainly increase the weight loss at high temperature because their size decreases little with increasing temperature. The borosilicate glass, as a sealent, can seal the coating cracks well and decrease greatly the weight loss at low temperature, but it nearly loses all ability of sealing defects at high temperature due to its low viscosity and low resistance to oxygen diffusion (Fig. 7). The SiC/Si-Zr coating increases the weight loss at low temperature although it makes the composite gain weight at high temperature. Furthermore, the rapid weight gain indicates that the SiC/Si-Zr coating has a low resistance to oxygen diffusion, and then both the oxidation protection temperature and time of the coating are limited. If the defects could be sealed completely, the composite with the multi-layer SiC coating would have a weight gain at high temperature and a lower weight loss at low temperature. Because SiC has an excellent resistance to oxygen diffusion, the multi-layer SiC coating free from the deposition defects could work at higher temperature and would be long-time.

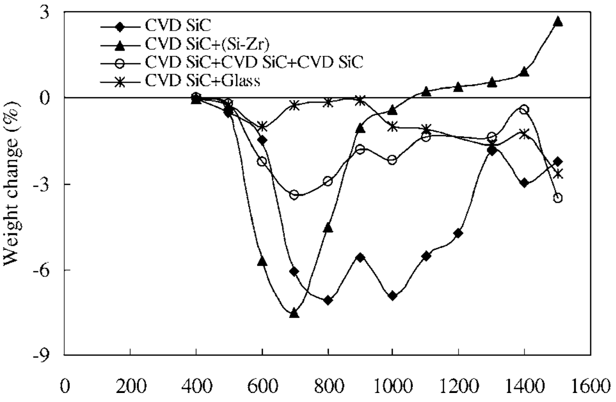


Figure 7 Relations of weight change to temperature of the C/SiC composite with different coatings after oxidation for 5 hours.

The spherical particles of SiC aggregate were transformed from the liquid droplets. The condensation of the vapor in the boundary would occur if the supersaturation degree reaches the critical value, and lead to the formation of liquid droplets composed of Si, C, Cl and H. The contents of both Cl and H were decreased and stoichiometric SiC aggregates were eventually obtained as the liquid droplets moved to the surface of the substrates in the boundary layer because the temperature became higher near the direction of the deposition substrates [8]. When deposition at 1000°C, it is very difficult for the as-formed liquid droplets to fuse together. As the droplets transform to the particles, removing of Cl and H contracts the particles. As a result, gullies were formed at the boundary between the particles. With increasing the deposition temperature, it was easier for the as-formed liquid droplets to fuse together. When deposition at 1300°C, few gullies could be formed because most of the as-formed liquid droplets were fused together. However, increasing the deposition temperature led to increasing the thermal mismatch between the coating and the substrates. This indicates that increasing the deposition temperature will increase the weight loss of the composite with a multi-layer SiC coating at low temperature as it decreases the weight loss at high temperature.

The particle size of SiC aggregate is very sensitive to the deposition pressure. When the deposition pressure is low enough, the supersaturation degree will not reach the critical value and liquid droplets will not be formed in the boundary around the substrates. At this condition, the controlling step of the deposition process is transformed from the liquid nucleation to the solid nucleation. The nucleation of SiC aggregates on the substrates is non-spontaneous due to the fast vapor diffusion in the very thin boundary. The non-spontaneous nucleation makes the SiC particles very small. With lowering the deposition pressure, the particle size will be decreased and the density of the SiC film will be increased. When the SiC aggregates become nanometer particles, the SiC film will be completely dense and free from deposition defects. However, the deposition rate of the SiC layer is greatly lowered with lowering the deposition pressure. It should be noted that nucleation of the SiC aggregates directly from the vapor is impossible at low temperature. As an oxidation protection coating, it should have a certain thickness to resist the oxygen diffusion. Depositing in the form of nanometer particles is too slow to prepare the oxidation protection coating. In the current article, the deposition rate at 5 kPa and 1000°C was 1 μm/h. Appropriately increasing the deposition temperature and decreasing the deposition pressure will not change obviously the deposition rate, but it will seal the net-defects better.

If there are interlayer gaps, sealing the net-defects will have not greatly effect on the oxidation protection property of the coating. Even though the net-defects are removed, oxygen can get in from the supporting defects in the outer layer, diffuse along the gaps and arrive eventually at the supporting defects in the inner layer. According to the supersaturation change, the deposition process on the fibers and the PyC interlayer can be defined in two stages. At the initial stage, the supersaturation in the boundary is lower than its critical value and a fine crystallite interlayer can be observed. As the deposition proceeds, the supersaturation reaches its critical value in a short time, which results in the formation of liquid droplets. The surface of the inner SiC layer will be inactivated by the elements O, Cl and S adsorbed on it before the outer SiC layer is deposited. When depositing the outer layer, solid nucleation on the inner layer will be difficult due to the inactivation, and then the fine crystallite interlayer can not be found. As the deposition proceeds, liquid nucleation takes place. Because the particles from the droplets can not be fused together with the inner layer, a gap is formed between the two layers.

Removing the gaps is very necessary in order to increasing the oxidation protection property of a multi-layer SiC coating. If there are not the interlayer gaps in a multi-layer coating, the preparation defects can be completely sealed and the net-defects will not decrease greatly the oxidation protection property. Clearly, increasing the deposition temperature and decreasing the deposition pressure will be favorable to sealing the gaps. In principle, depositing alternatively different layers, such as SiC and Si_3N_4 layer, can remove the net-defects in the multi-layer coating.

4. Conclusions

1. There existed two kinds of preparation defects in the CVD SiC coating on a C/SiC composite, including the supporting defects and the machining defects. The former were produced by supporting of the specimens and then were generally located at edges and corners of the specimens, the later were produced from the matrix pores formed between the fiber bundles after machining.

2. There existed two kinds of deposition defects in the multi-layer CVD SiC coating, including the plane-defects and the net-defects. The former were formed between the layers and then were very large in two-dimension, the later were produced at the boundaries between the particles due to the contraction and the incomplete fusion of SiC aggregate particles transformed from the liquid droplets.

3. Increasing the coating thickness could seal the machining defects, but it could not seal the supporting defects. Multi-deposition could not completely seal the preparation defects because the deposition defects became the channels of oxygen diffusion connecting the preparation defects, Although it decreased remarkably the weight loss of the composite.

4. The fully dense Si-Zr outer layer makes the composite gain weight at high temperature by sealing defects in the multi-layer, but it increases the weight loss at low temperature, and furthermore has a low resistance to oxygen diffusion. The borosilicate glass can decrease greatly the weight loss at low temperature by sealing the coating cracks, but it nearly loses all ability of sealing defects at the high temperature due to its low viscosity and low resistance to oxygen diffusion.

5. The preparation defects can be completely sealed if there exist no plane-defects in the multi-layer coating. Increasing the deposition temperature and decreasing

the deposition pressure will be favorable to removing the palne-defects. Depositing alternatively different layers, such as SiC and Si_3N_4 layer, can remove the net-defects in the multi-layer coating.

Acknowledgments

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