Thermal Expansion and Oxidation of 3D C/SiC Composites with Different Coatings from Room Temperature to 1400°C

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ABSTRACT

3D C/SiC composites with different CVD SiC coating and a bulk CVD SiC material were prepared by low pressure chemical vapor infiltration/deposition and the effects of oxidation and heat treatment on the thermal expansion of the composites were investigated. The expansion behavior of the composites can be changed by their coating thickness. The thicker the coating, the more largely it can be changed. When the coating is thick enough, it cannot be changed. The oxidation at 700°C and the heat treatment at 1400°C can decrease the interfacial bonding strength of the composites, and then their thermal expansion behavior is similar to that of the bulk CVD SiC. The longitudinal CTE of the composites is decreased and then increased by the oxidation at 700°C with increasing the weight loss. The effect of heat treatment is not related to the coating thickness besides the temperature. The oxidation and the heat treatment at 1400°C has a similar effect on the expansion behavior of the composite with four-layer coating, but has a completely different effect on that of the composite with two-layer coating above 1000°C.

Key Words: Carbon fiber composites, Oxidation, Thermal expansion, Heat treatment

1. INTRODUCTION

Carbon fiber reinforced silicon carbide composites (C/SiC) have been developed and tested for structural applications such as the components of turbine engines, the reentry thermal protection system of spacecraft, ultra-lightweight mirrors and so on /1,2/. Coefficient of thermal expansion (CTE) is one of the most important properties for all these applications.

The fibers, matrix and interlayer in C/SiC composites have different CTEs, and then interfacial thermal stress will be produced in the composites. Clearly, the expansion behavior of the composites depends upon the interfacial thermal stress /4/, which can be changed by oxidation and heat treatment. The oxidation decreases the interfacial stress by reaction of PyC and oxygen, and the heat treatment transforms the interfacial stress distribution by interfacial sliding and yielding. The coating thickness affects not only the oxidation resistance, but also the interfacial stress of the composite. Therefore, the thermal expansion of the composite can be related to the oxidation, the heat treatment and the coating thickness. Thus it is very important and necessary to understand the role of interfacial stress in C/SiC composites. Although the thermal expansion of C/SiC composites has been reported and a few data can be obtained /3/, the effects of oxidation and heat treatment on the thermal

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expansion of the composites have not been investigated.

In this article, 3D C/SiC composites with different CVD SiC coating and a bulk CVD SiC material were prepared and the thermal expansion of the composites, after oxidation at different temperatures and after heat treatment for different times, was investigated.

2. EXPERIMENTAL PROCEDURES

2.1 Fabrication of the specimens

Three-dimensional (3D) preforms were braided by a four-step method using 3K T-300 carbon fibers and deposited with both PyC and SiC to fabricate a 3D C/SiC composite using butane and methyltrichlorosilane (MTS). The deposition conditions of PyC interlayer were as follows: temperature 960°C, pressure 5KPa, time 20 hours, Ar flow 200ml·min^{-1}, butane flow 15ml·min^{-1}. The deposition conditions of SiC matrix were as follows: temperature 1000°C, pressure 5KPa, time 120 hours, H_2 flow 350ml·min^{-1}, Ar flow 350ml·min^{-1}, and the molar ratio of H_2 and MTS 10. Specimens along the fiber axial were machined from the fabricated composites and further deposited with SiC under the same conditions. Three kinds of CVD SiC coating were prepared by multi-deposition. They consisted of one layer, two layers and four layers respectively, each layer being about 20μm in thickness.

The deposition conditions of the bulk SiC material were as follows: temperature 1100°C, time 200 hours, H_2 flow 400ml·min^{-1}, Ar flow 400ml·min^{-1}, and the molar ratio of H_2 and MTS 3-5. Although the deposition conditions of the SiC bulk material was different from those of the SiC matrix and the SiC coating, measuring its CTE is necessary to investigate the effect of the heat treatment on expansion behavior of the composites.

2.2 Measurements of CTE

A DIL 402C dilatometer made by NETZSCH Company was employed for measurements of CTE. The required specimen size was 3.5×3.5×20 mm^3. Oxidation tests were conducted in air at 700°C and 1400°C. All measurements were conducted in nitrogen atmosphere from room temperature to 1400°C. Some specimens were measured three times. The first measurement acted on the second one as a heat treatment, as did the third one on the second one.

3. RESULTS AND DISCUSION

3.1 Effect of CVD SiC coating on CTE

The relations of longitudinal CTE to temperature of 3D C/SiC with different CVD SiC coating were compared with that of the bulk CVD SiC in Fig. 1. Although the coating and the matrix were deposited at 1000°C, they were cracked by the thermal stress at different temperatures. Fig. 1 showed that the matrix cracking temperature was 880°C and the coating cracking temperature was 970°C. Because the PyC interlayer decreased the thermal mismatch, the former was lower than the latter. At the matrix cracking temperature, the longitudinal CTE reached a peak value. Below this temperature, the matrix expansion released the compressive stress in fibers and then the longitudinal CTE increased linearly with increasing temperature. From the matrix cracking temperature to the coating cracking temperature, it was decreased by the restriction of fibers. As a result, the longitudinal CTE reached a valley value at the coating cracking temperature. Above 970°C, high modulus of the SiC

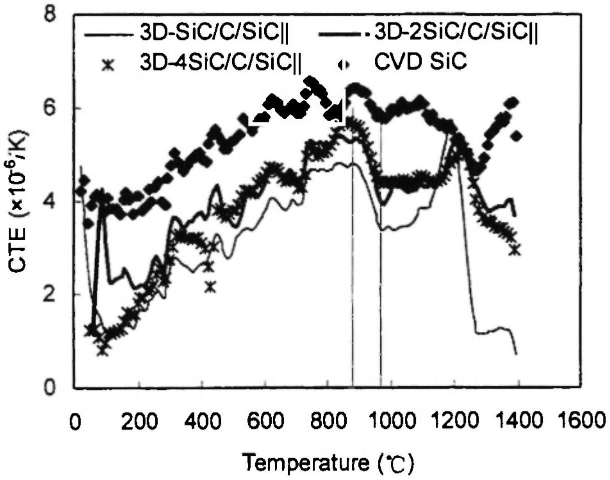

Fig. 1: Relations of longitudinal CTE to temperature of 3D C/SiC with different CVD SiC coating

matrix and the coating caused a high axial tensile stress in the fibers. The fibers were continually fractured by the stress and the expansion of SiC matrix was slowly released from 1000°C to 1200°C. Therefore, the longitudinal CTE reached another peak value after maintained in a temperature range. For the same reason, it decreased and then maintained from 1200°C to 1400°C. The matrix cracking temperature and the coating cracking temperature of 3D C/SiC determined by its relation of longitudinal CTE to temperature were fully identical with those determined by its relation of weight loss to temperature in air /5/.

Although the longitudinal CTE of C/SiC was related to thickness of the CVD SiC coating, the matrix cracking temperature and the coating cracking temperature were not changed by increasing layers of the coating. Below the matrix cracking temperature, the longitudinal CTE was obviously increased when the layers were increased from one to two, but it was not further increased when they were increased from two to four. It should be noted that the first peak values on the relations of longitudinal CTE to temperature were increased and the second peak values were decreased with increase in the layers. However, the temperatures corresponding to the second peak values were increased with increase in the coating layers. Furthermore, the second peak values at these temperatures were always equal to that of the bulk SiC because the restriction of fibers to expansion of SiC matrix disappeared. The thinner the coating, the more easily the coating can be compressed, the smaller the valley values, and then the more rapidly the coating expansion was released as the fibers were fractured. Consequently, the thicker the coating, the wider the temperature range in which the coating expansion and the fiber restriction were in balance, and the larger the longitudinal CTE in this temperature range.

3.2 Effect of oxidation on CTE at 700°C

Fig. 2 showed the relations of weight loss to temperature of 3D C/SiC with two-layer and four-layer coating after oxidation in air at 700°C. Obviously, the composite with two-layer coating lost weight more rapidly than that with four-layer coating. Oxidation started at the fiber-PyC interface uniformly and then progressed in the interlayer at 700°C because it was controlled by the reaction of PyC with oxygen. With increasing oxidation time, thickness of gaps between the fibers and the interlayer produced by oxidation was increased, the interfacial bonding strength was decreased, and then the expansion behavior of the composites was more similar to that of the bulk CVD SiC.

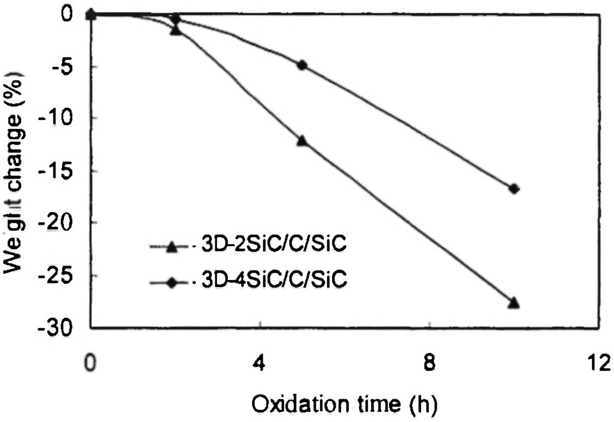

Fig. 2: Relations of weight loss to oxidation time of 3D C/SiC with different coating in air at 700°C

Fig. 3 showed the relations of longitudinal CTE to temperature of 3D C/SiC with two-layer coating after oxidation at 700°C for different times and Fig. 4 showed those with four-layer coating. After oxidation for two

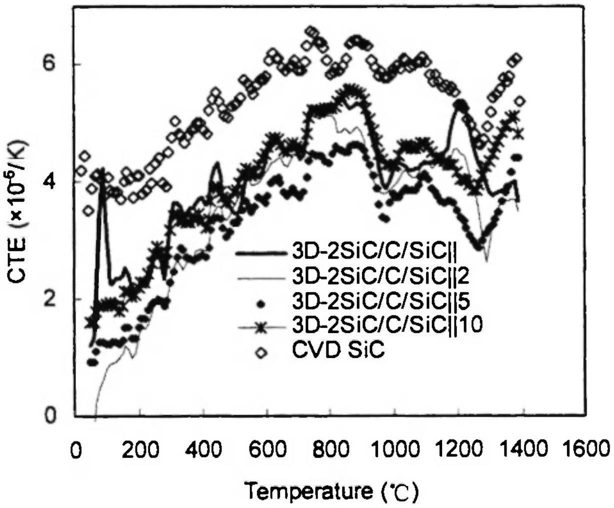

Fig. 3: Relations of longitudinal CTE to temperature of 3D C/SiC with two-layer coating after oxidation at 700 °C for different time

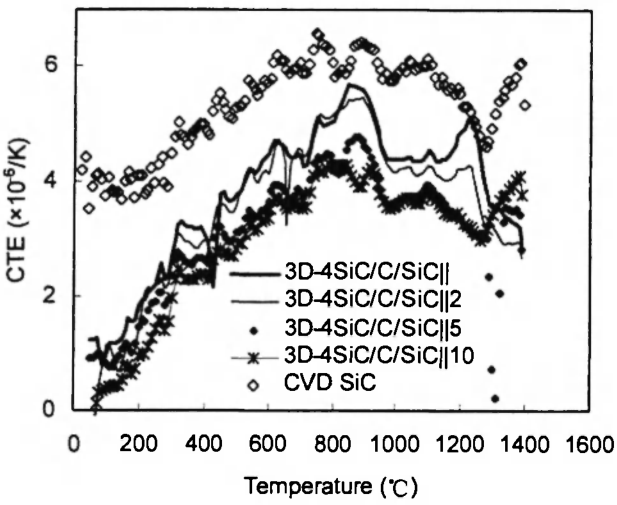

Fig. 4: Relations of longitudinal CTE to temperature of 3D C/SiC with four-layer coating after oxidation at 700 °C for different time

hours, the longitudinal CTE of the composite with two-layer and four-layer coating were lowered in the whole temperature range, and the second peak values nearly disappeared. This indicates that the interfacial bonding in the composite was weakened. After oxidation for five and ten hours, the interfacial bonding strength was so low that the expansion of the fibers no longer had any effect on the longitudinal CTE of the composite. As a result, the expansion behavior of the composite was controlled by the matrix and the coating, then the composite and the bulk CVD SiC reached a valley value at the same temperature which was about 1280°C. Because the matrix was porous, the CTE of the SiC matrix was lower than that of the bulk SiC.

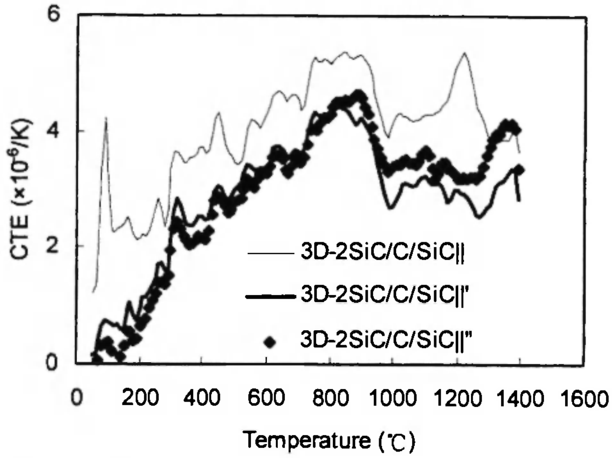

Fig. 5: Effect of heat treatment on the relation of longitudinal CTE to temperature of 3D C/SiC with two-layer coating

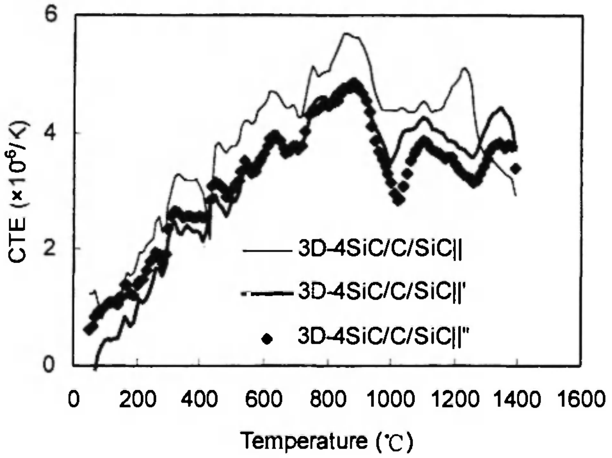

Fig. 6: Effect of heat treatment on the relation of longitudinal CTE to temperature of 3D C/SiC with two layer coating.

Fig. 5 showed the relations of longitudinal CTE to temperature of 3D C/SiC with two-layer coating from the first, the second and the third measurement and Fig. 6 showed those with four-layer coating. It can be seen that the longitudinal CTE after the oxidation was similar to that after the heat treatment, especially for the composite with four-layer coating. This indicates that the oxidation and the treatment had a similar effect on the composite. The former decreased the interfacial bonding strength in the composite by forming interfacial gaps, and the latter lowered it by producing interfacial slide. The gaps were produced by the uniform reaction of PyC with oxygen when oxidized in air at 700°C and the slide was caused by the high shear stress in treatment.

Comparing Fig. 3 and Fig. 4, it can be found that the oxidation had a different effect on the expansion behavior of the composites with different coating. For the composite with two-layer coating, the longitudinal CTE after oxidation for five hours was obviously lower than that after oxidation for ten hours. But for the composite with four-layer coating, the relation of longitudinal CTE to temperature after oxidation for five hours nearly coincided with that after oxidation for ten hours. Because the weight loss of the former was much larger than that of the latter, the interfacial bonding strength of the former was much lower than that of the latter and the expansion of SiC in the former was more free than in the latter. When cooled down from the measurement temperature after oxidation for five hours, the width of the matrix cracks in the former was smaller than that of the latter. As a result, the longitudinal CTE of the former after oxidation for ten hours was larger than that of the latter in the whole temperature range. This is apparently no accident because the treatment had a similar effect on the expansion behavior. For the composite with two-layer coating, the longitudinal CTE from the second measurement was obviously lower than that from the third measurement. But for the composite with four-layer coating, the longitudinal CTE from the second measurement was higher than that from the third measurement at high temperatures. This is difficult to explain exactly. For the second measurement, the longitudinal CTE of the former was obviously lower than that of the latter at high temperatures, but for the third measurement, the longitudinal CTE of the former was similar to that of the latter over the whole temperature range. This indicates that the treatment decreased the longitudinal CTE of 3D C/SiC with a CVD SiC coating, and the final decrease was not related to the coating thickness but related to the treatment temperature.

3.3 Effect of oxidation on CTE at 1400°C

Fig. 7 showed the relations of weight loss to temperature of 3D C/SiC with two-layer and four-layer coating after oxidation in air at 1400°C. It can be seen that the composite with two-layer coating lost weight more rapidly than that with four-layer coating. Because the oxidation was controlled by diffusion of oxygen through the coating defects, it was non-uniform. Fig. 8 shows the relations of longitudinal CTE to temperature of 3D C/SiC with different coating after oxidation at 1400°C for five hours. Obviously, the longitudinal CTE of the composite with two-layer coating was little different from that with four-layer coating at low temperatures, but they were completely different at high temperatures. The larger weight loss of the composite with two-layer coating essentially changed its expansion behavior. A reasonable explanation for this result is that modulus of the matrix at high temperatures was greatly decreased by the non-uniform oxidation compared with the interfacial bonding strength. At this condition, the expansion of the matrix could not resist restriction of the fibers, and then the longitudinal CTE of the composite always decreased at high temperatures. Formation of silica in the matrix and the cavities beneath the coating should be responsible for the modulus decrease. However, the expansion behavior of the composite with four-layer coating after the oxidation was very similar to that after the treatment. Because the

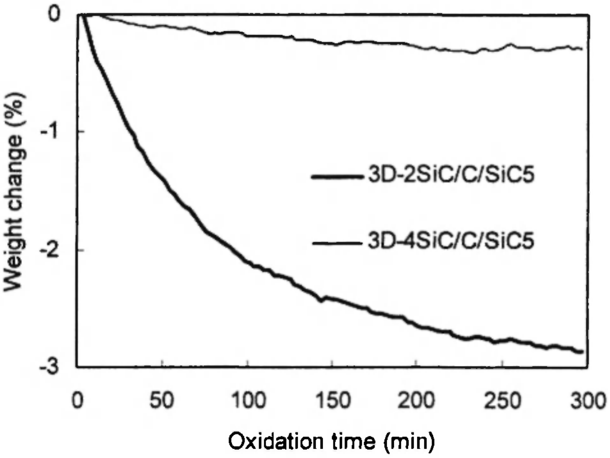

Fig. 7: Relations of weight loss to oxidation time of 3D C/SiC with different coating in air at 1400°C.

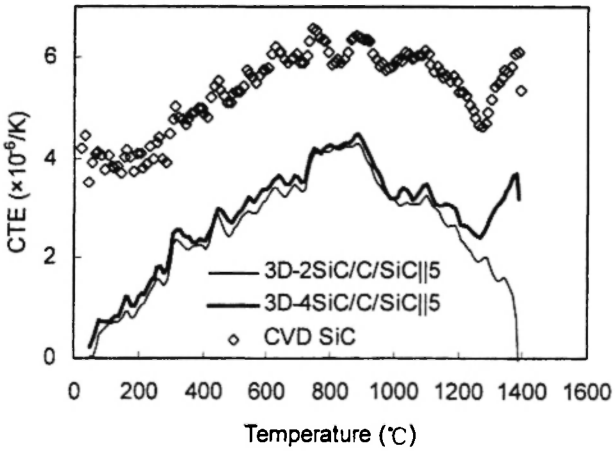

Fig. 8: Relations of longitudinal CTE to temperature of 3D C/SiC with different coating after oxidation at 1400°C for 5 hours.

weight loss was very low, microstructures of the composite with four-layer coating were almost unchanged and the oxidation had the same effect as the treatment on the longitudinal CTE.

4. CONCLUSIONS

1. The expansion behavior of the C/SiC composites can be changed by their coating thickness. The thicker the coating, the more largely it can be changed. When the coating is thick enough, it cannot be changed.
2. The oxidation at 700°C and the heat treatment at 1400°C can decrease the interfacial bonding strength of the C/SiC composites, and then their thermal expansion behavior is similar to that of a bulk CVD SiC.
3. The longitudinal CTE of the composites is decreased and then increased by the oxidation at 700°C with increasing the weight loss. The effect of heat treatment is not related to the coating thickness besides to the temperature.
4. The oxidation and the heat treatment at 1400°C has a similar effect on expansion behavior of the C/SiC composite with four-layer coating, but has a completely different effect on that of the composite with two-layer coating above 1000°C.

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