

Effects of interphase thickness and heat treatment on transverse thermal diffusivity of 3D C/SiC composites

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Three-dimensional C/SiC composites with different interphase thickness were fabricated by chemical vapor infiltration method, and transverse thermal diffusivity was measured in the temperature range 20 ~ 1400 °C using a laser flash technique. The diffusivity decreases initially with interphase thickness increasing from 30 nm to 100nm, whereas an increase is observed when interphase thickness increases from 100 nm to 200 nm. Heat treatment at 1400 °C improves the diffusivity of the composites, and yet it has little effect on the relationship between the diffusivity and interphase thickness.

Key words: C/SiC composites, Thermal diffusivity, Interphase thickness, Heat treatment.

Introduction

Carbon-fiber-reinforced silicon carbide (C/SiC) composites have been applied widely as thermostructural applications in the fields of aeronautics and astronautics due to their excellent performance, especially at high temperatures [1, 2]. PyC, as the interphase between C fibers and SiC matrix, can improve fracture toughness of C/SiC composites and make the composites behave in a noncatastrophic failure mode. Different performances were exhibited when the C/SiC composites were fabricated with various PyC interphase thickness [3-5]. It is believed that microstructural changes due to the variation of PyC interphase are of great significance to the performance of C/SiC composites. Moreover, heat treatment is an important technique to improve the properties of the materials and has certain effects on microstructure of the C/SiC composites. Therefore, an improved understanding about the role of interphase and heat treatment in microstructural changes of the composites will lead to the design and processing of the composites with reliable performance.

Thermal diffusivity of three-dimensional (3D) C/SiC composites is one of the most important properties for their applications, and it is greatly sensitive to the microstructural and compositional changes in the composites [6-11]. For the above purpose, the emphasis of this article is to investigate the dependence of transverse thermal diffusivity of 3D C/SiC composites on interphase thickness and heat treatment.

Experimental

Fabrications

Three-dimensional fiber preforms were prepared by braiding 3K T-300 carbon fibers in four-step method. The volume of fibers was 40%. The preforms were infiltrated with both PyC interphase and SiC matrix to fabricate C/SiC composites by low pressure chemical vapor infiltration method (LPCVI) using butane and methyltrichlorosilane (MTS). The infiltration conditions of PyC interlayer were as follow: temperature 960 °C, pressure 5 KPa, Ar flow 200 ml · min⁻¹, butane flow 15 ml · min⁻¹. The thickness was controlled by the infiltration time and could be calculated according to the weight gain [3]. The preforms with PyC interlayer were treated at 1800 °C for 1 hr in vacuum conditions before they were infiltrated with SiC matrix. The infiltration conditions of SiC matrix were as follow: temperature 1000 °C, pressure 5 KPa, time 120 hrs, H₂ flow 350ml · min⁻¹, Ar flow 350ml · min⁻¹, and the molar ratio of H₂ and MTS 10. A CVD SiC coating was prepared on the specimens which were machined from the fabricated composite in the size of $\Phi 12.7 \times 2.5$ mm³ under the same conditions as the SiC matrix. The porosity of the composites was about 13 ~ 15%. Five groups of 3D C/SiC composites were finally obtained, as listed in table 1.

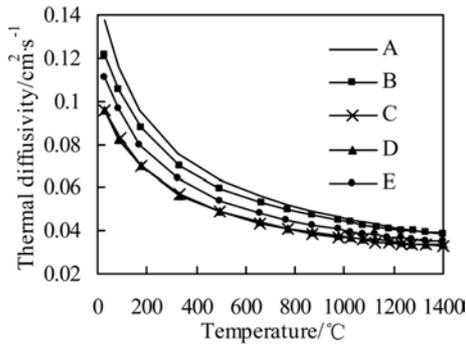
Measurements

Laser flash apparatus (LFA 427, NETZSCH Co.) was employed for measurements of thermal diffusivity of 3D C/SiC composites perpendicular to braided plies, i.e. transverse thermal diffusivity. All measurements were conducted in argon atmosphere at different temperatures from room temperature to 1400 °C. Thermal diffusivity at each appointed temperature was measured three times. In order to investigate the effect

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Table 1. Prepared 3D C/SiC composites with different interphase thickness.

Materials	A	B	C	D	E
Interphase Thickness/nm	31	66	98	129	194

**Fig. 1.** The dependence of transverse thermal diffusivity on temperature for 3D C/SiC composites with different interphase thickness.

of heat treatment on thermal diffusivity, all specimens were measured three times under the same measurement conditions.

Results and Discussion

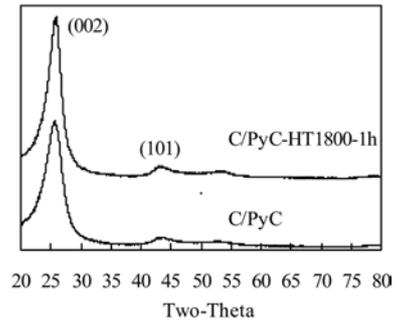
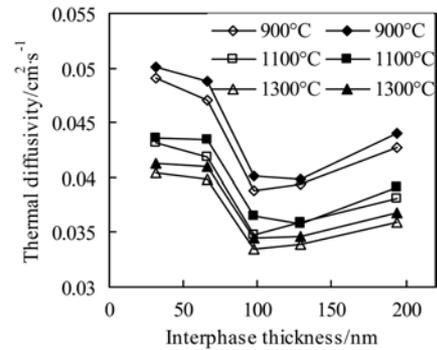
Transverse thermal diffusivity of 3D C/SiC composites

Transverse thermal diffusivity data are plotted as a function of temperature in Fig. 1 for 3D C/SiC composites. It can be seen that the transverse thermal diffusivity of all 3D C/SiC composites decreases monotonically with increasing temperature. The curves can be well fitted by power functions over the full temperature range. As an example, the transverse thermal diffusivity of Material A can be described by the following equation:

$$\alpha_A = \frac{48.39}{T^{1.058}} + 0.02041 \quad (1)$$

where α is the transverse thermal diffusivity of the composites and T is the Kelvin temperature. This differs from the earlier research [10], in which the preforms infiltrated with PyC interphase were never treated at 1800 °C during the fabrication process. In that case, it decreased initially with temperature increasing, and then increased at high temperatures. The equation fitting those data included an exponential term besides the two terms in Eq.(1). Additionally, the transverse thermal diffusivity of 3D C/SiC composites studied in this work is higher than that in Ref.10.

To interpret this difference, XRD analysis was carried out to the C/PyC preforms with and without heat treatment at 1800 °C for 1 h. As shown in Fig. 2, the diffraction angles 2θ are around 25° and 43°, which are assigned to disordered graphitic (002) plane and (101) plane, respectively. The average interlayer

**Fig. 2.** XRD of C/PyC preforms with and without heat treatment.**Fig. 3.** The dependence of transverse thermal diffusivity on interphase thickness for 3D C/SiC composites at typical temperatures. Open (closed) symbols indicate the first (second) measurement.

spacing d_{002} and the crystallite dimensions $L_{c(002)}$ of treated C/PyC are 3.471 Å and 4.57 nm. The untreated C/PyC has d_{002} (3.488 Å) and $L_{c(002)}$ (3.69 nm). The results indicate that treated C/PyC has higher graphitization degree than untreated one, shortening of interlayer spacing and largening of crystallite dimensions. Moreover, XRD analysis to the two kinds of C/SiC composites shows that the crystallite dimensions of SiC infiltrated in treated C/PyC preforms are larger than those of SiC infiltrated in untreated C/PyC preforms, which indicates that grain growth of SiC is affected by the microstructure of C/PyC preforms. The larger the crystallite dimensions are, the higher the thermal diffusivity is. Therefore, the increase of the transverse thermal diffusivity of 3D C/SiC composites and the disappearance of the exponential term in this work should be attributed to the microstructural change of C fiber and PyC interphase caused by heat treatment for C/PyC preforms.

Effect of interphase thickness on transverse thermal diffusivity of 3D C/SiC composites

To clarify the relationship between transverse thermal diffusivity and interphase thickness of 3D C/SiC composites, data from different groups at typical high temperatures (900 °C, 1100 °C and 1300 °C) are plotted as a function of interphase thickness in Fig. 3. It can be seen that the diffusivity changes with various interphase thickness in a non-monotonic way and the curves

behave in a similar way. It decreases initially with increasing interphase thickness, and then an increase follows. Material A with 30 nm thick interphase displays the highest diffusivity, and Material C with 100 nm thick interphase has the lowest one.

For 3D C/SiC composites, transverse thermal diffusivity is influenced by the volume fraction of the individual components, as well as by the microstructure of the composites. For the tested specimens in this study, the volume fraction of PyC becomes higher with interphase thickness increasing. Interfacial debonding and sliding occur more easily at the interface region because of a relatively weaker interface, and then more thermal gaps are formed. The degradation of the interfacial bond strength induces a corresponding decrease in the phonon mean-free-path, which will lead to the reduction in the interface conductance. All of these factors, which are derived from the increase of PyC interphase, tend to lower the transverse thermal diffusivity of 3D C/SiC composites.

However, microcracks perpendicular to the axis of fiber bundles are usually produced in SiC matrix because of thermal stress caused by thermal expansion mismatch between C fiber and SiC matrix. The matrix cracks play a role in the thermal diffusivity of the composites. As Yin et al [3] researched, the matrix cracking stress, σ_m , increases with interphase thickness increasing. For the fiber-reinforced composites,

$$\sigma_m = \left[\frac{6\tau_s\Gamma_m f^2 E_f E^2}{(1-f)E_m R} \right]^{1/3} - \frac{qE}{E_m} \quad (2)$$

where, τ_s is the interfacial shearing strength; Γ_m is the matrix fracture energy; f is the volume fraction of fibers; E_f , E_m , E is the elastic modulus of fiber, matrix and the composite, respectively; R is the radius of fiber; q is the residual stress in matrix [12]. For the

tested specimens in this study, it is assumed that τ_s is equal because sliding usually happens in the interphase. And then σ_m depends on q . The thermal stress caused by thermal expansion mismatch of C fiber and SiC matrix can be released partially by deformation of PyC interphase, which has a low modulus, and by debonding at the interface region. The residual stress in matrix decreases gradually with the interphase thickness increasing [13], which results in the decrease of the amount of matrix cracks, as shown in Fig. 4. Evidently, the more microcracks exist in SiC matrix, the lower transverse thermal diffusivity of the composites.

From the above, it can be concluded that for 3D C/SiC composites, the initial decrease of transverse thermal diffusivity is dominated by the increase of PyC interphase with the interphase thickness increasing from about 30 nm to 100 nm, whereas the diffusivity increases with the interphase thickness increasing from 100 nm to 200 nm because the benefit of the decrease of microcracks in SiC matrix outweighs the loss from PyC interphase.

Effect of heat treatment on transverse thermal diffusivity of 3D C/SiC composites

The measured composites are considered to have been heat treated at 1400 °C in argon atmosphere. Therefore, the results of the second measurement may display the effect of heat treatment on transverse thermal diffusivity of 3D C/SiC composites. The data are a little larger than the first results, as shown in Fig. 3, which indicate that heat treatment can improve transverse thermal diffusivity of 3D C/SiC composites, while the diffusivity of heat-treated composites still decreases monotonically with increasing temperature, as shown in Fig. 5. The temperature dependence of transverse thermal diffusivity of heat-treated Material A can be described by the following equation:

$$\alpha'_A = \frac{55.41}{T^{1.073}} + 0.02032 \quad (3)$$

This indicates that heat treatment at 1400 °C doesn't

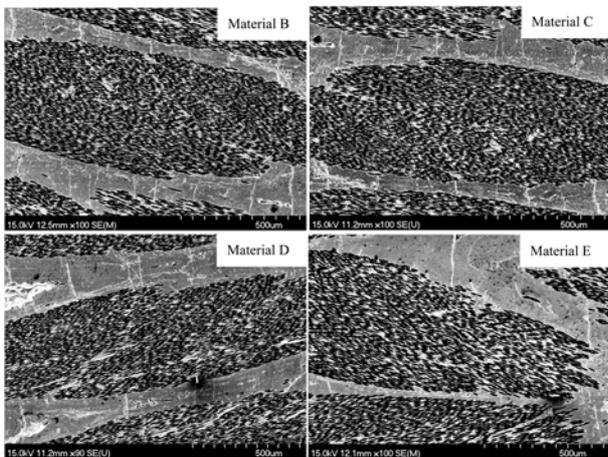


Fig. 4. SEM micrographs of the polished section parallel to the fiber bundles for 3D C/SiC composites to illustrate the decreasing crack density in the matrix with the interphase thickness increasing.

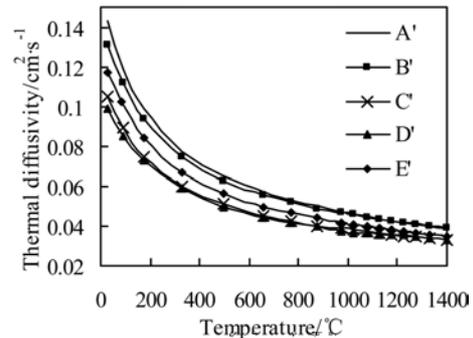


Fig. 5. The dependence of transverse thermal diffusivity on temperature for heat-treated 3D C/SiC composites with different interphase thickness.

change the regulation except the values. The curves of two measurements intersect at 1400 °C which was the treatment temperature. It is believed that the microstructural changes in the composites caused by heat treatment are non-reversible. No changes would occur in C fiber and PyC interphase since the treatment temperature is lower than that of heat treatment for C/PyC preforms. Then, the increase of transverse thermal diffusivity of heat-treated C/SiC composites should be attributed to the change in SiC matrix. The treatment leads to the increase of microcracks in SiC matrix, which would lower the diffusivity. However, it also leads to the grain growth and the decrease of crystal defects in CVD SiC matrix, which would raise the diffusivity. It can be concluded that the latter factors dominate since the diffusivity is improved finally. Moreover, the results of the third measurement are exactly equal to the second, which indicates that a permanent structural change occurs in the composites.

From Fig. 3, it can be seen that the dependences of the diffusivity on interphase thickness for 3D C/SiC composites in two measurements are similar. This indicates that heating to 1400 °C has little effect on the relationship between transverse thermal diffusivity and interphase thickness for 3D C/SiC composites.

Conclusions

The effect of interphase thickness and heat treatment on thermal diffusivity of 3D C/SiC composites was investigated and the conclusions were summarized. For 3D C/SiC composites fabricated by CVI method, the temperature dependence of transverse thermal diffusivity can be well fitted by a power function over the full temperature range. The diffusivity changes with various interphase thickness in a non-monotonic way. The initial decrease of transverse thermal diffusivity is dominated by the increase of PyC interphase with interphase thickness increasing from about 30 nm to 100 nm, whereas the diffusivity increases with interphase thickness increasing from 100 nm to 200 nm because

the benefit of the decrease of microcracks in SiC matrix outweighs the loss from PyC interphase. Heat treatment can improve the thermal diffusivity of 3D C/SiC composites, whereas it has little effect on the relationship between the diffusivity and interphase thickness.

Acknowledgments

The authors acknowledge the financial support of Natural Science Foundation of China (Contract No.51302220) and National Young Elitists Foundation (Contract No.50425208), and Fundamental Research Foundation (Contract No.JC20120204), Program for Changjiang Scholars and Innovative Research Team in University.

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