Oxidation behaviors of carbon fiber reinforced multilayer SiC–Si₃N₄ matrix composites

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Abstract: Oxidation behaviors of carbon fiber reinforced SiC matrix composites (C/SiC) are one of the most noteworthy properties. For C/SiC, the oxidation behavior was controlled by matrix microcracks caused by the mismatch of coefficients of thermal expansion (CTEs) and elastic modulus between carbon fiber and SiC matrix. In order to improve the oxidation resistance, multilayer SiC–Si₃N₄ matrices were fabricated by chemical vapor infiltration (CVI) to alleviate the above two kinds of mismatch and change the local stress distribution. For the oxidation of C/SiC with multilayer matrices, matrix microcracks would be deflected at the transition layer between different layers of multilayer SiC–Si₃N₄ matrix to lengthen the oxygen diffusion channels, thereby improving the oxidation resistance of C/SiC, especially at 800 and 1000 °C. The strength retention ratio was increased from 61.9% (C/SiC–SiC/SiC) to 75.7% (C/SiC–Si₃N₄/SiC/SiC) and 67.8% (C/SiC–SiC/Si₃N₄/SiC) after oxidation at 800 °C for 10 h.

Keywords: carbon fiber reinforced SiC matrix composites (C/SiC); multilayer SiC–Si₃N₄ matrices; elastic modulus mismatch; coefficient of thermal expansion (CTE) mismatch; oxidation resistance

1 Introduction

Carbon fiber reinforced SiC matrix composites (C/SiC) have been considered as a kind of promising high-temperature structural material [1–3]. They have great application potential in aero-engines, aircraft/high-speed train braking systems, and aerospace aircraft thermal protection systems due to the low density, excellent

mechanical properties, and thermal shock resistance [4–6]. Presently, the oxidation behaviors of C/SiC have been extensively studied. Due to the existence of cracks in matrix, oxygen can easily diffuse inside composites at intermediate temperatures (700–900 °C), leading to poorer oxidation resistance [7,8]. A lot of methods have been used to improve the oxidation resistance of C/SiC at intermediate temperatures, such as the applications of oxidation-resistant matrices, self-healing matrices, and oxidation-resistant coatings [9–11].

For C/SiC, due to the mismatch of coefficient of thermal expansion (CTE) and elastic modulus between

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carbon fiber and SiC matrix, the thermal residual stress (TRS, σ) would be formed during the cooling process from fabrication temperature to room temperature. It is well known that the TRS would cause microcracks in matrix, thereby providing diffusion channels for oxygen [12,13]. The oxygen will diffuse from cracks into carbon fibers, leading to the failure of the composites. Therefore, one way to improve the oxidation resistance of C/SiC is to reduce the CTEs and elastic modulus mismatch between the carbon fiber and the SiC matrix.

Si₃N₄ is a kind of noteworthy oxidation-resistant ceramic, and its CTEs and elastic modulus are generally higher than those of carbon fiber, but lower than those of SiC [7,14–19]. For example, as listed in Table 1, the axial and radial CTEs of carbon fiber are -0.72×10^{-6} – 2.0×10^{-6} K⁻¹ and 8×10^{-6} – 8.85×10^{-6} K⁻¹, respectively, and the CTEs of Si₃N₄ and SiC are 2.8×10^{-6} – 3.6×10^{-6} K⁻¹ and 3.5×10^{-6} – 4.9×10^{-6} K⁻¹, respectively. It is expected that the introduction of Si₃N₄ to SiC matrix will alleviate the CTE and elastic modulus mismatch between carbon fiber and SiC matrix, the same as the multilayer SiC/PyC matrix in C/SiC [20]. The optimization of CTE and elastic modulus mismatch is beneficial for the improvement of oxidation resistance. It is known to us that Si₃N₄ has better oxidation resistance than PyC. Meanwhile, when comparing the oxidation resistance of Si₃N₄ and SiC, it can be found that the activation energy of Si₃N₄ is generally higher than that of SiC, showing better oxidation resistance at high temperatures [21,22]. Therefore, the multilayer SiC–Si₃N₄ matrices can be used in C/SiC to improve the oxidation resistance.

In this study, the multilayer SiC–Si₃N₄ matrices were fabricated in C/SiC by chemical vapor infiltration (CVI). The oxidation properties of as-prepared C/SiC composites with multilayer matrices were investigated in static air at 800, 1000, and 1200 °C for 10 h. The evolutions of microstructure and mechanical properties in the oxidation process were revealed.

Table 1 CTEs of C_f, SiC, and Si₃N₄

Phase	C _f		Si ₃ N ₄	SiC
	Axial	Radial		
CTE, α (10 ⁻⁶ K ⁻¹)	(-0.72)–2.0 [7,14]	8–8.85 [7]	2.8–3.6 [15,16]	3.5–4.9 [17]

2 Experimental

2.1 Material preparation

Two-dimensional (2D) carbon fiber preforms (T300, 1K, Toray, Japan) were used as the reinforcements, which had been detailed in Ref. [23]. Firstly, PyC interphase with a thickness of about 200 nm was infiltrated into reinforcements by CVI process at 900 °C, and then was heat treated at 1800 °C for 2 h under vacuum [24]. After that, SiC matrix was infiltrated into preforms by CVI at 1000 °C for 300 h with a pressure of 10 kPa. The same as our previous studies, this CVI process used methyltrichlorosilane (MTS, CH₃SiCl₃) as the precursor, argon as diluting gas to control the rate of reaction, and hydrogen as the carrier gas [18,25]. The obtained porous C/SiC composites (1.9 g·cm⁻³, 12 vol% open porosity, as shown in the black area in Fig. 1) were processed into cuboids with fixed dimensions for further experiments. Sequentially, different multilayer matrices were alternately infiltrated into specimens by CVI, and the deposition sequences of multilayer SiC–Si₃N₄ matrices are shown in Fig. 1. Each SiC sub-layer was deposited for 60 h under the same conditions as above. The Si₃N₄ matrix was deposited with silicon tetrachloride (SiCl₄) and ammonia gas (NH₃) as the precursor, argon as the diluting gas, and hydrogen as the carrier gas at 800 °C for 60 h [26]. According to the different multilayer matrices, these composites were denoted as sample S0 (C/SiC–SiC/SiC), sample S1 (C/SiC–Si₃N₄/SiC/SiC), and sample S2 (C/SiC–SiC/Si₃N₄/SiC).

Fig. 1 Schematic deposition sequences of multilayer matrices for the as-prepared three composites processed by CVI.

2.2 Oxidation tests

The oxidation tests were carried out under static air in a tube furnace at 800, 1000, and 1200 °C for 10 h. At first, the tube furnace was heated to the given oxidation temperature, and then the samples were placed in corundum crucible and slowly pushed into the tube furnace for oxidation. After 10 h of oxidation, the crucible was slowly taken out and cooled to room temperature in air. In order to record the weight changes of these samples during the oxidation process, the weights before and after oxidation tests were measured by an analytic balance (AG 204, Mettler Toledo, Zurich, Switzerland). The weight changes of samples were calculated according to Eq. (1):

$$\Delta m = \frac{m - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 and m are the sample weights before and after oxidation tests, respectively, and Δm is the weight loss ratio. In order to ensure reliability, at least three samples were tested at each experiment.

2.3 Characterization

Open porosity and bulk density of these specimens were measured by the Archimedes drainage method. The microstructures of these composites were observed by the scanning electron microscope (SEM; Helios G4 CX, FEI, USA), the back-scattered electron imaging (BSE), and the spherical aberration corrected transmission electron microscope (TEM; Themis Z, FEI, USA). The element composition was examined by energy dispersive spectroscopy (EDS). The phase composition was identified by X-ray diffraction (XRD; X' Pert Pro, Philips, the Netherlands).

The flexural strength was tested by three-point bending method in the testing machine (CMT 4304, Sans, China) using specimens with dimensions of 40 mm × 5 mm × 3 mm. The loading rate and span were 0.5 mm·min⁻¹ and 30 mm, respectively.

Nanoindentation tests were performed on the finely polished cross-section of these composites in an *in-situ* nanomechanical test system (TI 980 triboindenter, Hysitron, USA) to measure Young's modulus and hardness of each component at nanoscale. During the test, the relative position of Berkovich diamond indenter and *in-situ* scanning probe microscopy (SPM) imaging mode was fixed, so that the diamond indenter could be accurately positioned to the test area which needed to be indented through the *in-situ* SPM imaging mode

such as carbon fibers and different matrices [27–30]. The half angle of Berkovich diamond indenter was 65.27°, and the ratios between projected area and the square of the indentation depth were equal to 24.5 [28]. In this study, all the nanoindentation tests were performed in a partial loading–unloading procedure, and the load-controlled mode was selected and the maximum load was set to 10 mN. During the testing process, more than five valid data points were obtained for each phase to assure the reliability of nanoindentation data. According to Oliver–Pharr method, Young's modulus of each selected component in nanoscale was extracted from the corresponding force–penetration depth curves [31]:

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (2)$$

where E and ν are Young's modulus and Poisson's ratio of each selected component, respectively, E_r is the reduced modulus, and E_i and ν_i are Young's modulus and Poisson's ratio of the Berkovich diamond indenter ($E_i = 1140$ GPa, $\nu_i = 0.07$), respectively.

3 Results and discussion

3.1 Microstructure and phase composition

The density and open porosity are 2.00 g·cm⁻³ and 9 vol% for C/SiC–SiC/SiC (sample S0), 2.20 g·cm⁻³ and 5 vol% for C/SiC–Si₃N₄/SiC/SiC (sample S1), and 2.12 g·cm⁻³ and 5 vol% for C/SiC–SiC/Si₃N₄/SiC (sample S2), respectively. Samples S1 and S2 exhibited higher density and lower open porosity than sample S0, owing to the introduction of multilayer SiC–Si₃N₄ matrices. Figure S1 in the Electronic Supplementary Material (ESM) shows the XRD pattern of the as-prepared three composites. It can be seen that these composites are composed of carbon and β-SiC. However, the Si₃N₄ matrix cannot be detected by XRD. It is because the Si₃N₄ prepared by CVI process is amorphous, which has been proved in Ref. [32].

As shown in Figs. 2(a)–2(c), multilayer matrices are deposited around carbon fiber bundles from inside to outside. The large inter-bundle pores in composites are caused by the “bottleneck effect” of CVI process. The cracks in matrix in the pristine samples are shown in Figs. 2(d)–2(f), and the pores in matrix can hinder the propagation of cracks through pinning and passivating effect. It can be observed that the cracks in these three pristine samples are tiny (as marked by the arrows in

Figs. 2(d)–2(f)). So, in subsequent oxidation tests, the effect of pristine pores and crack on different composites can be ignored. For samples S1 and S2, the multilayer matrices are evenly distributed and continuous, but the SiC matrix layer and Si₃N₄ matrix layer cannot be divided clearly in the low-magnification BSE images. The PyC interphase is shown in Fig. 2(g), and its thickness is about 200 nm. Figures 2(h) and 2(i) are SPM images recorded by nanomechanical test system of samples S1 and S2, and the thin dark gray Si₃N₄ matrix layer can be distinguished during the testing process. For sample S2, since the remaining space between the adjacent fiber bundles is already tiny after the deposition of Si₃N₄, the outermost SiC layer is thinner than sample S1.

For further analyzing the microstructure and confirmation of phase composition, Fig. 3 presents the high-magnification BSE images of the as-prepared composites. As shown in Figs. 3(a)–3(c), the SiC–Si₃N₄ multilayer matrices can be observed obviously in samples S1 and S2. The element composition of multilayer matrices can be proved by corresponding EDS images, as shown in Figs. 3(e) and 3(g). It was confirmed that the multilayer matrices were composed of SiC and Si₃N₄. The layer of Si₃N₄ matrix is evenly distributed, and is tightly combined with SiC matrix layers. It can also be

observed that a layer of Si₃N₄ matrix is especially thin, about 1.6 μm in thickness, which means that the content of Si₃N₄ matrix is quite low compared with SiC matrix. For samples S1 and S2, it can be found in Figs. 3(b) and 3(c) that the multilayer SiC–Si₃N₄ matrices are prepared in both two composites, but the distribution of Si₃N₄ matrix is different. The distances from Si₃N₄ matrix to carbon fiber bundles are about 7 and 13 μm in samples S1 and S2, respectively. It is consistent with the schematic of deposition sequences in Fig. 1. Meanwhile, the microstructures of the two CVI SiC layers were further observed by TEM. The high-angle annular dark-field scanning transmission electron microscopy (HADF-STEM) and the high resolution transmission electron microscopy (HRTEM) image and corresponding EDS mapping of two CVI SiC layers are shown in Figs. 3(h) and 3(i), respectively. The transition layer between two CVI SiC layers is composed of free carbon, SiC, and SiO₂. The presence of transition layer may be due to the transitory effects, which will inevitably occur at the end of the CVI process and during the regrowth of the CVI process. For the same reason, the EDS signal for Si passes through very pronounced minima at the transition layer because of the presence of transition layer between SiC and Si₃N₄, as shown in Figs. 3(e) and 3(g).

Fig. 2 Low-magnification and high-magnification BSE images of polished cross-sections of (a, d) sample S0, (b, e) sample S1, and (c, f) sample S2, respectively. (g) BSE images of the PyC interphase. The SPM images of (h) sample S1 and (i) sample S2 recorded by *in-situ* nanomechanical test system.

Fig. 3 BSE images of polished cross-sections of (a) sample S0, (b) sample S1, and (c) sample S2. High-magnification BSE images and corresponding EDS images of the marked scan lines of (d, e) sample S1 and (f, g) sample S2, respectively. (h) HAADF-STEM image and (i) HRTEM image and corresponding EDS mapping of CVI SiC.

3.2 Oxidation behavior

At room temperature, the flexural strengths of these composites are 465 ± 12 MPa for sample S0, 460 ± 7 MPa for sample S1, and 419 ± 36 MPa for sample S2. The corresponding flexural stress–strain curves are shown in Fig. S2 in the ESM. All of these three composites are representative of non-catastrophic fracture behavior [33]. The flexural strength of samples S1 and S2 is similar to that of sample S0. Therefore, the C/SiC with multilayer SiC–Si₃N₄ matrices can still keep excellent mechanical properties at room temperature. For samples S1 and S2, the different distribution positions of Si₃N₄ matrix will lead to different stress distribution in the multilayer matrices, so that the flexural strength of samples S1 and S2 is different, as shown in Figs. 3(b) and 3(c). However, the difference between these two samples is slight, which is acceptable in the follow-up works. Meanwhile, as shown in Fig. S2 in the ESM, the flexural

modulus are 63 ± 1 GPa for sample S0, 52 ± 2 GPa for sample S1, and 49 ± 1 GPa for sample S2. It indicates that the porosity of samples S1 and S2 is slightly lower than that of sample S0, but the introduction of Si₃N₄ will make their stiffness lower than that of sample S0.

Oxidation behavior of these composites (samples S0, S1, and S2) was measured. Mainly chemical reactions of the as-prepared three composites, which might happen during oxidation, were listed according to the relevant Refs. [21,34,35]:

It can be found that the oxidation of carbon fiber and PyC interphase (Reaction (3)) leads to weight loss

and the others lead to weight gain. Thus, the weight loss of these composites represents the consumption of the carbon fiber and PyC interface, which will inevitably cause the decrease of mechanical properties. The initial temperature of passive oxidation of SiC (Reaction (4)) in static air is about 800 °C, which is a weight-increasing reaction and would reduce some of the oxidative weightlessness during the reaction progress. Meanwhile, the weight changes of Si₃N₄ phase (Reaction (5)) can be ignored because of the low content of Si₃N₄ matrix.

The weight changes of these three composites at different temperatures are shown in Fig. 4. As described above, the weight loss of C/SiC at 800 °C is mainly controlled by Reaction (3). As shown in Fig. 4(a), after oxidation for 10 h at 800 °C, the weight loss of sample S0 reaches 8.1%, which is significantly larger than those of samples S1 and S2, indicating the severe erosion of carbon fiber and PyC interphase. At 1000 and 1200 °C, samples S1 and S2 also show smaller weight changes than sample S0 (Figs. 4(b) and 4(c)). The total weight change of these composites after oxidation for 10 h at

different temperatures is shown in Fig. 4(d). It shows that the weight loss gradually decreases with the increase of oxidation temperatures, and decreases by only 0.9% and 0.3% for samples S1 and S2, respectively, while decreases by 4.1% for sample S0 at 1200 °C. The preparation temperature of SiC matrix is 1000 °C. As oxidative temperature increases, the cracks in matrices gradually close to decrease the diffusion rate of oxygen. These cracks close when the oxidation temperature reaches above 1000 °C. At this time, oxygen needs to diffuse through the SiO₂ layer on the material surface and the multilayer SiC–Si₃N₄ matrices before it can react with the carbon fibers. Therefore, the oxidation weight loss gradually decreases with the increase of temperature, reaching the lowest point at 1200 °C.

The residual flexural strength and strength retention ratio of the as-prepared three composites after oxidation are listed in Fig. 5. As shown in Fig. 5(a), obvious decrease of flexural strength can be found for these three composites after oxidation for 10 h at 800 °C, which is consistent with the severe weightlessness. The strength

Fig. 4 Weight changes of the as-prepared composites after the oxidation for 10 h at (a) 800 °C, (b) 1000 °C, and (c) 1200 °C. (d) Total weight change of the as-prepared three composites.

retention ratios after oxidation at 800, 1000, and 1200 °C are 61.9%, 71.4%, and 89.7% for sample S0, 75.7%, 81.3%, and 86.7% for sample S1, and 67.8%, 103.1%, and 90.2% for sample S2 (Fig. 5(b)), respectively. When the temperature is between 800 and 1100 °C, the oxidation is controlled by the diffusion of oxygen gas in the cracks [8,36]. As temperature increases, the matrix microcracks caused by TRS gradually close, and the opening width of these cracks will decrease. The difficulty of oxygen diffusion into materials will increase, thereby causing the raise of strength retention ratio of these three samples. When the temperature rised to 1200 °C, the oxidation is controlled by the diffusion of oxygen in SiO₂ layer [8,36]. For these composites, the oxidation only stays on the surface SiC, so that the strength retention ratios of these three samples are almost the same. Meanwhile, it can be notably seen that the strength retention ratios of samples S1 and S2 are higher than that of sample S0 after oxidation at 800 and 1000 °C, while they are almost the same for these samples at 1200 °C. The higher strength retention ratio and lower weight loss mean that multilayer SiC–Si₃N₄ matrices are conducive to improving the oxidation resistance of C/SiC, especially for the oxidation at 800 and 1000 °C.

Figure 6 shows the BSE images of the cross-sections of the as-prepared three composites after oxidation at 800 °C for 10 h. For sample S0, carbon fibers are oxidized seriously, and the damaged fibers are not evenly distributed, as shown in Fig. 6(a). The carbon fibers close to the matrix (marked by the white circles) and intra-bundle cracks (marked by the yellow circles) were generally damaged. For samples S1 and S2, the damaged area of carbon fibers reduced, and the inner fibers were better preserved (Figs. 6(c) and 6(e)). It means

that, compared with sample S0, the volume fraction of carbon fibers in samples S1 and S2 is higher after oxidation, so that the fibers can bear the load more effectively.

Figures 6(b), 6(d), and 6(f) exhibit the crack propagation of samples S0, S1, and S2, respectively. For sample S0, without the introduction of Si₃N₄ matrix, the straight main cracks which are perpendicular to the fiber bundle expand from matrix to carbon fibers, as shown in Fig. 6(b). As shown above, the transition layer between two CVI SiC layers is composed of free carbon, SiC, and SiO₂. The existence of carbon will make the transition layer between different matrices to be a weak area, where the debonding can easily occur. The microcracks can deflect at the transition layer, but they do not affect the inward propagation of the main crack in sample S0. The straight cracks can provide the oxygen diffusion channels, and thereby the carbon fibers near to these cracks will be oxidized firstly and then reduce the oxidation resistance of C/SiC. However, for samples S1 and S2, as marked by the arrows in Figs. 6(d) and 6(f), matrix cracks can be deflected at the transition layer between different CVI matrices, which prolongs the crack propagation path and increases the difficulty of oxygen diffusion into the fiber bundles, thereby improving the oxidation resistance of C/SiC. Meanwhile, since the outermost SiC layer for sample S2 is thinner than S1, it will partly fall off due to the crack deflection (Fig. 6(f)). Compared with sample S1, removing the outermost SiC layer in sample S2 cannot play a protection function to inner carbon fibers, which is not conducive to the oxidation resistance. Thus, sample S2 has shown lower strength retention ratios than sample S1 at 800 °C, as shown in Fig. 5.

Fig. 5 (a) Residual flexural strength and (b) strength retention ratio of the as-prepared samples after oxidation for 10 h at different temperatures.

Fig. 6 BSE images of polished cross-sections of the as-prepared three composites after oxidation at 800 °C for 10 h: (a, b) sample S0, (c, d) sample S1, and (e, f) sample S2.

3.3 Evolution of oxidation mechanism

As previously studied, the oxidation kinetics of C/SiC depends on the oxidation temperature. When the temperature is below 800 °C, the diffusion rate of oxygen is faster than the reaction rate of carbon phase. Thus, the oxidation is controlled by the carbon/oxygen reaction. When the temperature is between 800 and 1100 °C, the oxidation is controlled by the diffusion of oxygen gas in the cracks. When the temperature is above 1100 °C, due to the formation of SiO₂ layer, the oxidation is controlled by the diffusion of oxygen in SiO₂ layer, and the oxidation only stays on the surface of the composites [8,36]. Thus, in the high-temperature oxidation environment at 800 and 1000 °C, the difficulty of oxygen diffusion in the matrix microcracks determines the oxidation properties of C/SiC composites.

For C/SiC, the microcracks in matrix are caused by the TRS (σ). The most commonly equation for TRS is Eq. (6):

$$\sigma = E_m \Delta T \Delta \alpha \quad (6)$$

where E_m is the modulus of the matrices in C/SiC, ΔT is the temperature difference between testing temperature and processing temperature, and $\Delta \alpha$ is the CTE difference between carbon fibers and matrices. It indicates that the production and propagation of matrix microcracks depend on the severity of CTE and elastic modulus

mismatch between carbon fiber and SiC matrix, thereby influencing the oxidation resistance of C/SiC.

As shown above, Table 1 lists the order of CTEs of three phases in these as-prepared C/SiC with multilayer SiC–Si₃N₄ matrices. It can be found that α (carbon fiber along radial direction) > α (SiC) > α (Si₃N₄) > α (carbon fiber along axial direction). The CTE mismatch between carbon fibers and SiC-based matrices can be adjusted by the introduced Si₃N₄ matrix. In the multilayer SiC–Si₃N₄ matrix, the Si₃N₄ and SiC were prepared at different temperatures. The Si₃N₄ was synthesized at 800 °C. During the subsequent synthesis of SiC at 1000 °C, there will be higher local internal stresses in the interfaces of different matrices. Therefore, although the CTE of Si₃N₄ is only slightly lower than that of SiC and the Si₃N₄ occupies a small part in the multilayer matrix, the introduction of Si₃N₄ will change the local stress distribution in the multilayer matrix, thereby affecting the propagation of microcracks.

The Young's modulus and hardness in nanoscale of the different phases (carbon fiber, SiC, and Si₃N₄ matrices) for samples S1 and S2 were measured by *in-situ* nanomechanical test system. The corresponding results are listed in Table 2. The diamond indenter had been positioned precisely at a specified spot on the cross-sections of samples S1 and S2. The Poisson's ratio of each selected phase was confirmed according to Refs. [37–40], and the Young's modulus in nanoscale among these tables was calculated according to Eq. (2). Typical load–displacement curves of carbon fiber, SiC, and Si₃N₄ are depicted in Fig. 7. For all these phases, the curves present little fluctuation during loading–unloading procedure. Based on these testing data, it can be concluded that the order of Young's modulus of three phases in this study is as follows: E (SiC) > E (Si₃N₄) > E (carbon fiber). It should be noted that because of the different scale testing methods and the skin–core structure of carbon fiber, the Young's modulus in nanoscale cannot be compared with the tensile modulus which is tested at macroscale [41,42]. For samples S1 and S2, Si₃N₄ was introduced into different locations of the SiC-based matrices by adjusting the sequence of deposition of different matrices. The elastic modulus mismatch between carbon fibers and SiC matrices could be adjusted by the introduction of Si₃N₄, and then the multilayer SiC–Si₃N₄ matrices with gradient modulus were prepared in C/SiC. Meanwhile, it can be seen from Table 2 that the Si₃N₄ is apparently softer than SiC. Therefore, the introduction of Si₃N₄ will make

Table 2 Young's modulus and hardness in nanoscale of C_f, SiC, and Si₃N₄

Phase	Poisson's ratio, ν	Hardness in nanoscale (GPa)	Young's modulus in nanoscale, E (GPa)
C _f	0.30 [37]	6.1±0.4	50±7
SiC	0.21 [38]	42.0±2.0	441±27
Si ₃ N ₄	0.27 [39,40]	27.5±3.6	272±22

Fig. 7 Typical load–displacement curves of nanomechanical tests of carbon fiber (C_f), SiC matrix, and Si₃N₄ matrix.

the stiffness of samples S1 and S2 lower than that of sample S0, showing lower flexural modulus (Fig. S2 in the ESM).

Figure 8 shows the schematic diagram of oxygen diffusion channels for the as-prepared C/SiC composites at 800 and 1000 °C. For C/SiC without multilayer SiC–Si₃N₄ matrices, there are straight microcracks in SiC matrix, as shown in Fig. 8(a). Although the transition layer composed of free carbon and SiO₂ can deflect the cracks, it does not significantly extend the oxygen diffusion channels. Oxygen can easily diffuse into fiber bundles through these microcracks and react with the PyC interface and carbon fibers, causing serious oxidative

damage. For C/SiC with multilayer SiC–Si₃N₄ matrix (Fig. 8(b)), the introduction of Si₃N₄ matrix can alleviate the CTE and elastic modulus mismatch between carbon fiber and SiC matrix, and then change the local stress distribution in the multilayer matrix. As shown in Figs. 6(d) and 6(f), the microcracks can be deflected in the transition layer between different layers of the multilayer SiC–Si₃N₄ matrix, thereby providing longer diffusion channels for oxygen to diffuse from material surface into the fiber bundles. Therefore, the oxidation properties of C/SiC can be improved by the fabrication of multilayer SiC–Si₃N₄ matrix. 800 °C is the initial transformation oxidation temperature for C/SiC from carbon/oxygen reaction control to oxygen diffusion [43]. Thus, the oxidation properties of C/SiC at 800 °C can be promoted more obviously by the preparation of multilayer SiC–Si₃N₄ matrix, which is the same at 1000 °C. As for 1200 °C, the oxidation is controlled by the diffusion of oxygen in SiO₂ layer on the material surface [8], and the improvement of multilayer SiC–Si₃N₄ matrix to the oxidation resistance of C/SiC is not obvious. Therefore, the oxidation properties of C/SiC can be effectively improved by the multilayer SiC–Si₃N₄ matrices, especially at intermediate temperatures. In our follow-up studies, the distribution and content of Si₃N₄ layer in multilayer SiC–Si₃N₄ matrices need to be optimized to further improve the oxidation resistance of C/SiC.

4 Conclusions

In this study, multilayer SiC–Si₃N₄ matrices were introduced into C/SiC by CVI process, and then the oxidation behaviors of the as-prepared composites were

Fig. 8 Schematic diagram of the oxygen diffusion channels for C/SiC composites at 800 and 1000 °C: (a) without Si₃N₄ matrix and (b) with multilayer SiC–Si₃N₄ matrix.

investigated. The CTE and elastic modulus mismatch between carbon fiber and SiC matrix can be adjusted by the multilayer SiC–Si₃N₄ matrices, thereby changing the local stress distribution of matrices and deflecting the microcracks at the transition layer between different matrices during oxidation testing. For C/SiC–Si₃N₄/SiC/SiC and C/SiC–SiC/Si₃N₄/SiC, the deflected matrix microcracks would provide longer oxygen diffusion channels and then increase difficulty of the contact between oxygen and carbon fibers. Therefore, the carbon fibers can be better protected, and the oxidation resistance of C/SiC is improved by the multilayer SiC–Si₃N₄ matrices, especially at 800 and 1000 °C. After oxidation testing at 800 °C for 10 h, the strength retention ratios of C/SiC are increased from 61.9% (C/SiC–SiC/SiC) to 75.7% (C/SiC–Si₃N₄/SiC/SiC) and 67.8% (C/SiC–SiC/Si₃N₄/SiC).

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