The Effect of PyC/SiC Compound Interphase on the Properties of PIP SiC/SiC Composite

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Abstract. In order to improve the properties of SiC/SiC composite, chemical vapor infiltration (CVI) process was applied for fabricating the PyC/SiC compound interphase. Precursor infiltration and pyrolysis (PIP) process was used to fabricate SiC matrix. Then an investigation was carried out for the effect of PyC/SiC compound interphase thicknesses on the properties of the composites. According to the results, it was found that the mechanical properties of composites with the PyC/SiC compound interphase are much higher than those of composite with only PyC interphase. The flexural strength, flexural modulus, fracture toughness and interlaminar shear strength of the composites increase gradually when the thickness of CVI SiC interphase is lesser than 2 \( \mu \)m. Further increase of the thickness of CVI SiC interphase to 4 \( \mu \)m leads to a continuous increase on the modulus of the composites, while a decrease trend occurs on the flexural strength, fracture toughness and interlaminar shear strength of the composites because of the different coefficients of thermal expansion of the CVI SiC interphase and the PIP SiC matrix. SiC/(PyC/SiC\textsubscript{x})/SiC composites showed the better properties of oxidation resistance than those of SiC/PyC/SiC composite. It was due to the survived PyC interphase protected by CVI SiC interphase when the oxygen diffuses into the compound PyC/SiC\textsubscript{x} interphase.

1. Introduction

The potential of the silicon carbide fiber reinforced silicon carbide matrix composites (SiC/SiC) for application in the aviation and aerospace fields are extensive because they have a lot of outstanding advantages as high-temperature structural materials, such as lower density, higher temperature capability, excellent creep resistance, sufficient toughness[1-5]. Various processes are applied for fabricating SiC/SiC composites, such as chemical vapor infiltration (CVI), precursor infiltration and pyrolysis (PIP), reactive melt infiltration (RMI), nano infiltration transient eutectic (NITE) processes [6-10]. Compared with other processes, the major advantages of such PIP process are intrinsic homogeneity of SiC matrix at the atomic level, in terms of large class complex shapes components, lower processing temperatures, since the SiC precursors could be transformed into amorphous covalent SiC ceramic at initial temperatures higher than 800°C. Solid Polycarbosilane (PCS) with a ceramic yield of 60–70% is commonly used as polymer precursor for the SiC matrix. However, PCS needs to use xylene as a solvent to form a precursor solution with moderate viscosity and fluidity to impregnate the fiber perform. Therefore, the impregnation efficiency of PCS is relative low, which prolonging the preparation cycles of SiC matrix composite. With the development of high efficient
polymer pre-ceramics, a low viscosity castable liquid precursor without dilution required with a high SiC ceramic yield of 70%–80% has been adopted for SiC matrix composites by PIP process[11,12]. Meanwhile, it is well known that the mechanical behavior of SiC/SiC composites is dominantly influenced by the interphase between the fiber and matrix. Pyrolytic carbon (PyC) with layered crystal structures is the most common and effective interphases for SiC/SiC composites[13, 14]. However, due to the modulus and fracture energy of PyC interphase and PIP SiC matrix are comparatively lower than those of SiC fiber, and the PyC interphase is prone to oxidation at high temperatures resulted in the decrease of the mechanical properties of composites. A PyC/SiC compound interphase fabricated by chemical vapor infiltration process (CVI) may be more suitable for this kind of SiC/SiC composite and the mechanical properties and oxide resistance of the composite may be further improved with the PyC/SiC compound interphase. Hence, it is a necessary to design and fabricate a suitable interphase for this type of SiC/SiC composites.

The objective of this program is to study the effect of PyC/SiC compound interphase on the properties of PIP SiC/SiC composite, such as flexural strength, flexural modulus, fracture toughness and shear strength. The SiC interphase thicknesses were controlled by chemical vapor deposition time. It should be noticed that, in the most advanced fiber reinforced ceramic matrix composites, the thickness of interphases may be generally less than 1 μm. In this study, although the thickness of CVI SiC is greater than 1 μm, it also can be named as the SiC interphase due to the volume fraction of SiC interphase is far lower than those of PIP SiC matrix.

2. Experiment

The two dimensional (2D) preforms including 40% SiC fiber volume fraction were prepared with plain woven cloths made from KD-II 1K SiC fiber tows (National University of Defense Technology, Changsha, China). The SiC plain woven cloths were braided in Yi xing Xin li High Technology Co. Ltd., China. Prior to the SiC matrix densification process, the fiber performs were coated with pyrolytic carbon (PyC)/silicon carbide (SiC) compound interphase, i.e. PyC, PyC/SiC30h, PyC/SiC50h and PyC/SiC70h by chemical vapor infiltration (CVI) process, where the subscript following PyC/SiCx indicate the SiC chemical vapor deposition time. Propylene was used as the precursor of PyC and the argon as dilute gas. The PyC process temperature is 900°C for 144 h at reduced pressure of 5kPa in a CVI reactor. The thickness of PyC interphase in all of the composites is about 200nm. Methyltrichlorosilane (MTS), hydrogen and argon were applied for preparing the SiC interphase. SiC interphase was prepared at 1000°C with a reduced pressure of 5 kPa with a molar ratio of 10 between H2 and MTS, which was carried by bubbling hydrogen gas phase and argon as the dilute gas to slow down the chemical reaction rate during deposition. The thickness of SiC interphase was controlled by the deposition time, which was 0h, 30h, 50h and 70h respectively. Then, the SiC matrix was fabricated used a liquid precursor (Institute of Chemistry Chinese Academy of Sciences, Beijing, China) by PIP process at 1000°C in nitrogen atmosphere. The flow chart for preparation of 2D SiC/SiC composites was shown in Figure 1.

The procedure of continuous impregnation and pyrolysis was repeated till the weight gain rate of the SiC/SiC composites were less than 1%. The basic properties of the constituent in the composites were listed in table 1.

![Figure 1. Flow chart for preparation of 2D SiC/SiC composites.](image-url)
Table 1. Basic properties of the constituent in the composites[15-19].

| Constituent      | Coefficients of thermal expansion (×10^6/K) | Modulus (GPa) | Fracture energy (J/m²) |
|------------------|---------------------------------------------|---------------|-----------------------|
| KD-II SiC fiber  | 4.5                                         | 220           | 20                    |
| PyC              | 5.57                                        | 35            | 2~6                   |
| CVI SiC          | 4.5                                         | 350           | 6                     |
| PIP SiC          | 3                                           | 60-90         | <6                    |

The values of density and open porosity were obtained by the Archimedes drainage method using the deionized water as medium. The formulas for calculating the density \( \rho \) and open porosity \( P \) of composites are as follow:

\[
\rho = \frac{m_1 \rho_l}{m_3 - m_2} \tag{1}
\]

\[
P = \frac{m_3 - m_1}{m_3 - m_2} \times 100\% \tag{2}
\]

Where, \( \rho_l \) is the deionized water density, \( m_1 \) is the dry sample mass, \( m_2 \) is the floating weight of sample in the liquid, \( m_3 \) is the deionized water immersed weight of sample with dry surface.

The dimensions for flexural test samples, fracture toughness test samples and interlaminar shear test samples were shown in figure 2. The flexural test and flexural modulus were carried out following the guideline of ASTM standard C1341[20]. The fracture toughness test was followed the single edge notched beam (SENB) test procedure with the crosshead speed of 0.5 mm/min. The interlaminar shear test was according to ASTM C1292[21]. At least five samples were tested for each composite.

![Figure 2](image-url)

Figure 2. The dimensions of (a) flexural strength test samples, (b) fracture toughness test samples and (c) interlaminar shear test samples.

The formula for calculating flexural strength \( \sigma_f \), flexural modulus \( E_f \), fracture toughness \( K_{IC} \) and interlaminar shear strength \( \tau \) are as follow:

\[
\sigma_f = \frac{3FS}{2WH^2} \tag{3}
\]
$$E_f = \frac{KS^3}{4WH^3}$$  \hspace{1cm} (4)

$$K_{IC} = \frac{3FS}{2WH^2} a^{1/2} f\left(\frac{a}{H}\right)$$  \hspace{1cm} (5)

$$f\left(\frac{a}{H}\right) = 1.93 - 3.07\left(\frac{a}{H}\right) + 13.66\left(\frac{a}{H}\right)^2 - 23.98\left(\frac{a}{H}\right)^3 + 25.22\left(\frac{a}{H}\right)^4$$

and

$$\tau = \frac{F}{WB}$$  \hspace{1cm} (6)

Where $F$ is the maximum load during the test, $S$ is the span (30mm in this paper), $W$ is the width of the specimen, and $H$ is the thickness of the specimen, $a$ is the notch depth, $B$ is slot width.

The oxidation tests of SiC/SiC composites were performed in a alumina tube furnace at 1200°C for 5h, and then the oxidized samples were taken out of the furnace and cooling down naturally to room temperature. The remaining ratios of the strength were calculated from the strengths before and after oxidation treatment. Field emission scanning electron microscopy (FE-SEM, Hitachi’s S-4800 FE, Japan) was employed to examine morphology of the composites.

3. Results and discussion

3.1. Microstructure of the as-received composites

Some residual pores unavoidably existed in the composites owing to the “bottleneck effect” during CVI and PIP process[22]. The densities and open porosity for different kinds of composites are shown in Figure 3. The values of density and porosity for SiC/PyC/SiC composite with only PyC interphase are also included for comparison.

![Figure 3](image)

**Figure 3.** The density and open porosity for different kinds of composites.

Figure 3 reveals that the densities of SiC/(PyC/SiC$_x$)/SiC composites increased gradually with the deposition time of CVI SiC interphase because the density of CVI SiC is greater than that of PIP SiC, as shown in table 1. The open porosity of the composites with the compound (PyC/SiC$_x$) interphase are decreased gradually with the increased deposition time of CVI SiC interphase. A uniform thickness PyC interphase with about 200nm could be seen in the SiC/PyC/SiC composites, as shown
in figure 4a. The thickness of PyC interphase was the same in both of SiC/PyC/SiC and SiC/(PyC/SiC_3)/SiC composites because the same deposition time of the PyC. After 30h, 50h and 70h deposition of SiC interphase, the thickness of SiC interphase was about 0.5 μm, 2 μm and 4 μm, respectively, as shown in figure 4b, 4c and 4d. The thickness of SiC interphase increased with the increase of deposition time is not linear which is due to the deposition of SiC interphase need nucleation on the surface of PyC interphase at the initial period of deposition time.

![Image](Figure 4. The interphase morphologies images of different composites, for (a) SiC/PyC/SiC, (b) SiC/(PyC/SiC_30h)/SiC, (c) SiC/(PyC/SiC_50h)/SiC, (d) SiC/(PyC/SiC_70h)/SiC composites.)

3.2. Mechanical properties of the as-received composites

The mechanical properties of different kinds of composites are listed in table 2. It can be clearly seen that the flexural strength, flexural modulus, fracture toughness and interlaminar shear strength were significantly affected by the PyC/SiC interphase on the SiC fibers. The mechanical properties of composites with PyC/SiC interphase are higher than those of the SiC/PyC/SiC composites with only PyC interphase. To be more precise, flexural modulus, fracture toughness of the composites increased with the extension of CVI SiC deposition time. However, when the SiC deposition time increased from 50h to 70h, which means the thickness of SiC interphase increased from 2μm to 4μm (Figure 4c and 4d), the flexural strength and interlaminar shear strength of SiC/(PyC/SiC_70h)/SiC composite decreased comparing with those of SiC/(PyC/SiC_30h)/SiC and SiC/(PyC/SiC_50h)/SiC composites.

![Table 2. The mechanical properties of different kinds of composites](Table 2. The mechanical properties of different kinds of composites)

| Composites          | Flexural Strength/MPa | Flexural Modulus/GPa | Fracture Toughness/MPa×m−1/2 | Interlaminar shear strength/MPa |
|---------------------|-----------------------|----------------------|-----------------------------|--------------------------------|
| SiC/PyC/SiC         | 396±17                | 55±12                | 17.5±3                      | 21±3                           |
| SiC/(PyC/SiC30h)/SiC| 455±20                | 61±10                | 18.9±2                      | 24±2                           |
| SiC/(PyC/SiC50h)/SiC| 504±23                | 68±9                 | 20.7±3                      | 28±1                           |
| SiC/(PyC/SiC70h)/SiC| 433±27                | 72±11                | 25±0.5                      | 23±3                           |
Figure 5 depicts the typical stress-displacement curves for SiC/PyC/SiC, SiC/(PyC/SiC_{30h})/SiC, SiC/(PyC/SiC_{50h})/SiC and SiC/(PyC/SiC_{70h})/SiC composites. The curves have a linear range initially, and essentially nonlinear later. However, the fracture displacement decreased with the thickness increase of SiC interphase as shown in figure 5. It can be found that the fracture behavior of SiC/SiC composites can be tailored through the compound PyC/SiC interphase between the SiC fiber and PIP SiC matrix. Hence, the mechanical properties of the composites are closely related to the interphase, meanwhile the performance of the interphase is also closely related to basic physical performance of the constituents in the composites.

![Figure 5](image1.png)

**Figure 5.** The stress-displacement curves of SiC/PyC/SiC, SiC/(PyC/SiC_{30h})/SiC, SiC/(PyC/SiC_{50h})/SiC and SiC/(PyC/SiC_{70h})/SiC composites.

![Figure 6](image2.png)

**Figure 6.** The fracture morphologies of SiC/PyC/SiC(a), SiC/(PyC/SiC_{30h})/SiC(b), SiC/(PyC/SiC_{50h})/SiC(c) and SiC/(PyC/SiC_{70h})/SiC(d) composites.
Figure 6 shows the fracture morphologies of SiC/PyC/SiC, SiC/(PyC/SiC<sub>30h</sub>)/SiC, SiC/(PyC/SiC<sub>50h</sub>)/SiC and SiC/(PyC/SiC<sub>70h</sub>)/SiC composites. It could be seen that the SiC fibers pull length of SiC/PyC/SiC composite were longer than those of SiC/(PyC/SiC<sub>30h</sub>)/SiC, SiC/(PyC/SiC<sub>50h</sub>)/SiC and SiC/(PyC/SiC<sub>70h</sub>)/SiC composites, and the SiC fibers pull length were decreased with the increased thickness of CVI SiC interphase. This results were agree with the fracture displacement of the four kinds of composites as shown in figure 5.

The SiC/PyC/SiC composite with a weakly bonded PyC interphase because the modulus and fracture energy of PyC interphase and PIP SiC matrix are lower than that of KD-II SiC fiber, as shown in table 1. Premature failure of PyC interphase under flexural loading result in the SiC/PyC/SiC composite showing obvious nonlinear characteristic, as shown in figure 5. However, the modulus and fracture energy of CVI SiC is higher than those of the KD-II SiC fiber, PyC interphase and PIP SiC matrix. The higher mechanical properties of PyC/SiC interphase in composites must be attributed to the mixing rule of composite comparing with the SiC/PyC/SiC composite. However, the higher mechanical properties of PyC/SiC interphase in composites tends to increase the KD-II SiC fiber/PIP SiC matrix bonding strength and decrease the fracture displacement. In addition, the coefficients of thermal expansion mismatch between the constituents must also be considered, as shown in table 1. The coefficient of thermal expansion of PIP SiC matrix was lower than that of CVI SiC interphase, consequently residual tensile stresses may be expected between the PIP SiC matrix and CVI SiC interphase after cooling down from the processing temperature to room temperature. Noticeably, this residual tensile stresses may increase with the increased thickness of CVI SiC interphase, which resulted in the obvious debonding between the CVI SiC interphase and PIP SiC matrix, as shown in figure 7. On the contrary, no debonding phenomena between the CVI SiC interphase and PIP SiC matrix is found in SiC/(PyC/SiC<sub>30h</sub>)/SiC and SiC/(PyC/SiC<sub>50h</sub>)/SiC composites, which is the main reason for the decrease of flexural strength and interlaminar shear strength for SiC/(PyC/SiC<sub>70h</sub>)/SiC composite, even though the flexural modulus of SiC/(PyC/SiC<sub>70h</sub>)/SiC composite still present increasing trend, when compared with those of SiC/(PyC/SiC<sub>30h</sub>)/SiC and SiC/(PyC/SiC<sub>50h</sub>)/SiC composites.

3.3. Oxidation properties of the as-received composites

The weight loss and strength retention of four kinds of composites after 5h oxidation at 1200°C was shown in figure 8. SiC/PyC/SiC composites exhibit weight loss (-0.5%) and the strength retention was 85%. However, SiC/(PyC/SiC<sub>30h</sub>)/SiC, SiC/(PyC/SiC<sub>50h</sub>)/SiC and SiC/(PyC/SiC<sub>70h</sub>)/SiC composites show weight gain and the strength retention are all higher than 95%, and the strength retention has an increasing trend with the increase of the CVI SiC interphase.
Figure 8. The weight loss and strength retention of four composites after 5h oxidation at 1200°C.

The weight change during oxidation should consider the oxidation of constitutes. The oxidation of PyC interphase led to the weight loss, the oxidation of SiC interphase and SiC fiber resulted in weight gain and the reaction considering 1200°C oxidized temperature according to the following equations [23, 24]:

\[ 2C + O_2 \rightarrow 2CO \]  \hspace{1cm} (7)
\[ SiC + \frac{3}{2} O_2 \rightarrow SiO_2 + CO \]  \hspace{1cm} (8)

Besides, weight change of the composites during oxidation was also related to the defects existing in the composites. Pores and microcracks in SiC matrix could be seemed as a connected network of passageways for the inward diffusion of oxygen and the outward diffusion of the gaseous oxides at the tested temperatures. However, compared with SiC/PyC/SiC composite, the CVI SiC interphase in the SiC/(PyC/SiC_{30h})/SiC composites played a role of protecting the PyC interphase when the oxygen diffuses into the compound PyC/SiC_x interphase, as shown in figure 9, in which SiC/(PyC/SiC_{30h})/SiC composite as an example was shown in figure 9b. Hence, the survived PyC interphase protected by CVI SiC interphase is the main reason for the oxidation weight gain and higher strength retention of the SiC/(PyC/SiC_{30h})/SiC composites.

Figure 9. The interphase morphologies of SiC/PyC/SiC (a) and SiC/(PyC/SiC_{30h})/SiC composites after oxidation at 1200°C for 5 h in air.
4. Results and discussion
Various 2D SiC/(PyC/SiC_x)/SiC composites with different PyC/SiC interphase were prepared by PIP process. The composites with the PyC/SiC compound interphase possess a greater density and better mechanical properties, including the flexural strength, flexural modulus, fracture toughness and interlaminar shear strength, when compared with those of SiC/PyC/SiC composite.

The PyC/SiC compound interphases lead to better mechanical properties of the 2D SiC/(PyC/SiC_x)/SiC composites when the thickness of SiC interphase is lower than 2 μm. The flexural strength, fracture toughness and interlaminar shear strength would be decreased along with a further increasing of the thickness of SiC interphase to 4 μm. This negative effect should be attributed to thermal expansion mismatch between the CVI SiC interphase and the PIP SiC matrix, which means the residual thermal stress has a significant influence on the performance of the composites.

SiC/(PyC/SiC_x)/SiC composites showed the better properties of oxidation resistance than those of SiC/PyC/SiC composite. It was due to the survived PyC interphase protected by CVI SiC interphase when the oxygen diffuses into the compound PyC/SiC_x interphase.

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