Effect of infiltration time on the microstructure and mechanical properties of C/C-SiC
composite prepared by Si-Zr10 alloyed melt infiltration

Yonggang Tong ^{a, 1}, Shuxin Bai ^a, Qing H Qin ^b, Hong Zhang ^a, Yicong Ye ^a

^a College of Aerospace Science and Engineering, National University of Defense

Technology, Changsha, PR China

^b Research School of Engineering, College of Engineering and Computer Science,

Australian National University, ACT, Australia

Abstract: Low cost C/C-SiC composites were prepared through reactive melt infiltration with Si-Zr10 alloy infiltrant under different infiltration time. Effect of infiltration time on the microstructure and mechanical properties of the composite were investigated. ZrC tended to be formed in the composite and the amount of carbon phase decreased with an extension in the infiltration time according to the X-ray diffraction results. Phase transformation of the C/C-SiC composite was analyzed based on C-Si-Zr phase diagram. Flexural strength of the composite prepared by preform 0.9 g/cm³ decreased with an increase in the infiltration time while that of the composite prepared by preform 1.38 g/cm³ increased initially and then decreased reversely. The highest flexural strength of the composite was found at about 324 MPa. Flexural strength of the composite is considered to depend on its phase composition and fiber-matrix interface.

¹ Corresponding author. Tel.: +86 731 4573145; fax: +86 731 4574791.
E-mail address: tygiaarh419@163.com (YG.Tong).

Keywords: C/C-SiC composite; infiltration time; Microstructure; Mechanical properties; reactive melt infiltration

1. Introduction

Carbon fiber reinforced C, SiC binary matrix composite (C/C-SiC) has attracted much attention for its low density, high hardness, excellent oxidation resistance, high strength and thermal shock resistance [1-3]. It is a potential candidate for highly demanding engineering applications such as heat shields, structural components for reentry space vehicles, high performance brake discs and high temperature heat exchanger tubes [4].

Reactive melt infiltration (RMI) has been demonstrated to be an effective method to prepare C/C-SiC composite. Its advantages include short fabrication period, low cost and near net shape [5-8]. During the RMI process, liquid silicon or silicon based alloyed melt infiltrates into a porous C/C preform under the driving force of capillary. The molten melt expands to fill the pores and reacts with the carbon in the porous C/C preform, which ultimately results in a dense matrix. It should be mentioned that infiltration time is a very important parameter in the RMI process [9, 10]. The porous C/C preform can not be completely infiltrated by the molten melt if the infiltration time is too short, while overmuch infiltration time may lead to the excessive reaction of carbon with the melt, which may cause a negative effect on the mechanical properties of the resulting composite. An optimal infiltration time is critical for the composite's microstructure composition and mechanical properties. In the literature, Jiang et al [9] investigated the effects of the carbon matrix type and the infiltration

temperature on the infiltration behavior of molten Si and preparation of C/C-SiC composites. Nelson et al [11] studied the parameters of RMI through numerical simulation. Wang et al [12] evaluated the influence of infiltration time and temperature on the microstructure and properties of a low temperature derived C/ZrC composites. However, the effect of infiltration time on microstructure and mechanical properties of C/C-SiC composite by Si-Zr alloyed RMI have not yet been well understood so far.

In our previous study [13], C/C-SiC composite was prepared by a quick and economical RMI with a Si-Zr10 alloyed infiltrant. The composite was composed of SiC, ZrSi₂, C and ZrC and presented excellent oxidation resistance and high flexural strength. The aim of the present work is to evaluate effects of infiltration time on the microstructure and mechanical properties of C/C-SiC composites fabricated by Si-Zr10 alloyed melt infiltration.

2. Experimental

Carbon fiber needled felts were used as preforms. The carbon fibers were PAN-based (T300, Toray, Japan). The needled felts were prepared by a three-dimensional needling technique, starting with repeatedly overlapping the layers of 0° non-woven fiber cloth, short-cut-fiber web and 90° non-woven fiber cloth with needle-punching step by step. Pyrolytic carbon was deposited on the carbon fibers to form the porous C/C preforms by chemical vapor infiltration (CVI). Two kinds of C/C preforms with low and high pyrolytic carbon content were used in the RMI process, which were labeled as P1 (density 0.9 g/cm³) and P2 (density 1.38 g/cm³) respectively.

The porous C/C preforms were cut, polished, ultrasonically cleaned with ethanol and dried at 100°C for 4 h in an oven. C/C-SiC composite was then produced by infiltrating C/C preforms with Si-Zr alloyed melt (Zr: 10 at.%, Si: 90 at.%) at 1450-1500°C for different time. The details of RMI process can be found in [13].

The apparent density and open porosity of the composite were measured by Archimedes's method. Flexural strength was determined using a three-point-bending test in which specimens of 50 mm×10 mm×4 mm with 40 mm span is subjected to 0.5 mm/min crosshead speed. The morphologies of the composite were observed by a Hitachi-S4800 scanning electron microscope (SEM). The chemical composition was examined using an energy dispersive spectroscopy (EDS). The phases in the composite were identified by X-ray diffraction (XRD, Rigaku D/Max 2550VB-) using a Ni-filtered Cu K α radiation at a scanning rate of 5°/min and scanning from 20° to 80° of 2 θ .

3. Results and discussion

3.1 Phase composition and microstructure of C/C-SiC composite

Fig.1

Fig.2

Fig.1 shows the XRD patterns of the C/C-SiC composite prepared using different RMI time with C/C preform P2. The composites prepared for 1 and 2 h are composed of C, SiC and ZrSi₂ phases while the composites prepared for 3 and 4h are composed

of C, SiC, ZrSi₂ and ZrC phases. It indicates that ZrC tends to be formed in the composite with the extension of infiltration time. The intensity of carbon diffraction peaks also decreases with the increase of the infiltration time, which indicates more carbon consumption used in RMI process. The composite prepared using different infiltration time with C/C preform P1 presents the similar phase transformation (see Fig.2). The composites prepared for 1, 2 and 3h are composed of C, SiC, Si and ZrSi₂ and the composite prepared for 4h is composed of C, SiC and ZrC. The appearance of Si phase is resulted from the lower pyrolytic carbon content and larger porosity of preform P1. Table 1 shows the pyrolytic carbon content and open porosity of preform P1 and P2. For preform P1, the carbon volume fraction is 18.6% and the open porosity is 49.4%, which means the volume fraction of infiltrated Si-Zr melt will be larger than that of reaction carbon. Thus, there may be some residual Si-Zr melt in the composite prepared for limited infiltration time and Si phase diffraction peaks were found in the XRD analysis. Compared with preform P1, P2 has much larger reaction carbon content and less porosity. The infiltrated Si-Zr melt can react with pyrolytic carbon completely even in a very limited infiltration time period, such as 1 hour, and thus, Si in the alloyed melt was completely changed into SiC or ZrSi₂ phase.

The XRD analysis of C/C-SiC composites prepared by either preform P1 or P2 demonstrates the formation of ZrC phase and consumption of carbon with the extension of the infiltration time. Such phase transformation reveals the phase evolution of the composite prepared for different infiltration time, which can be discussed based on Si-Zr-C ternary phase diagram (Fig.3 [14]). Since the zirconium

content in the alloyed melt is just 10%, the resulting composite should contain a zirconium content of less than 10 %, which means that the phases of the resulting composite change in the area labeled in Fig.3. Preform P1 has a low reaction carbon content and large porosity. The amount of infiltrated Si-Zr alloyed melt is much larger than that of reaction carbon. The final phase composition of the C/C-SiC composite is located in the upper area of Si-ZrSi₂-SiC, demonstrating that the resulting composite is composed of Si, ZrSi₂ and SiC phases, which is consistent with the results from XRD analysis (Fig.2). The phase carbon in the XRD analysis refers to carbon fibers and the un-reacted carbon. With the extension of infiltration time, more and more carbon consumes by the reaction of carbon with silicon and the carbon content in the Zr-Si-C system increases. The phase composition of the resulting composite transfers in the direction marked by the arrow in the labeled area, which is from the area of Si-ZrSi₂-SiC to the area of ZrC-ZrSi₂-SiC and finally reaches to the area of ZrC-SiC-C with ZrC, SiC and C phases (the same as the results from XRD analysis for the composite for 4h infiltration). For the preform P2, there is a high carbon content and small porosity. The amount of infiltrated alloyed melt is less than that of reaction carbon and it can react with carbon completely in a short time period, such as 1 h. The final phase composition of the resulting C/C-SiC composite may be located in the area of ZrC-ZrSi₂-SiC and the reaction-formed phases in the resulting composite are ZrC, ZrSi₂ and SiC, which can be confirmed by the XRD analysis results from our previous work [13]. However, the zirconium content is very low in the alloyed melt (10%) and the amount of ZrC resulted from the reaction between

carbon and zirconium may be also very low, which is hardly to be detected by XRD analysis. That may be the reason why ZrC was not found in the XRD results of C/C-SiC composite prepared by preform P2 with infiltration time for 1 and 2 h. Considering the un-reacted carbon and carbon fibers, the phases in the resulting composite prepared by preform P2 is C, ZrC (hardly to be detected by XRD for short infiltration time), ZrSi₂ and SiC. Unfortunately, this is not a phase composition in equilibrium state as ZrSi₂ can react with the residual carbon in the composite. The reaction of ZrSi₂ with carbon is as follows:

Thermodynamics calculation was conducted to estimate the direction of this reaction (Fig.4). The changes in Gibbs' free energy reveal that the above reaction is strongly favored thermodynamically at infiltration temperature. Therefore, as the infiltration time increases, the reaction-formed ZrSi₂ can react with carbon in the composite and thus, ZrC and SiC phases are formed. The longer the infiltration time is, the more the ZrC phase is formed. That is why the intensity of ZrC diffraction peaks becomes stronger along with the extension of infiltration time (Fig.1). It is believed that all the ZrSi₂ phase will change into ZrC and SiC phases if infiltration time is longer enough and consequently, the final phase composition of the resulting C/C-SiC composite will be carbon, SiC and ZrC phases.

Fig.3

Fig.4

Fig.5

Fig.5 shows the cross-section SEM micrographs of the composites prepared for different infiltration time with C/C preform P1. As can be seen, the composites prepared for different infiltration time show dense morphologies with few pores. When increasing infiltration time, the amount of Si phase decreases and ZrC tends to be formed. The reaction-formed SiC distributes around pyrolytic carbon in the C/C preform while ZrSi_2 and Si locate in the central area of pores in the preform surrounded by the reaction-formed SiC. Because of the large open porosity, the alloyed melt infiltrates into not only the pores in the inter-fiber bundles but also the pores in the intra-fiber bundles. Some carbon fibers in the intra-fiber bundles are siliconized due to the reaction between carbon fibers and the infiltrated alloyed melt (Fig.6). However, no siliconized carbon fibers were observed in the composite prepared for different infiltration time with C/C preform P2 (Fig.7). Because of the high carbon content and low open porosity, the pores in the intra-fiber bundles are filled with pyrolytic carbon during chemical vapor infiltration of C/C preform. The alloyed melt mainly infiltrates into the pores in inter-fiber bundles. The reaction-formed SiC distributes around pyrolytic carbon on the edges of the carbon fiber bundles and ZrSi_2 locates in the middle area of the inter-fiber bundles surrounded by SiC. The pores in the intra-fiber bundles are filled with pyrolytic

carbon, which effectively protects carbon fibers from being damaged during alloyed melt infiltration.

Fig.6

Fig.7

3.2 Mechanical properties of the C/C-SiC composites

Fig.8

Fig.8 shows flexural strength of the resulting C/C-SiC composite prepared by RMI for different infiltration time. Flexural strength of the composites prepared using preform P1 decreases with an extension of infiltration time while that of the composites prepared using preform P2 increases initially and then decreases reversely. The highest flexural strength of the composite prepared by preform P2 for 2 h is about 324 MPa.

It is believed that the flexural strength of the composites is concerned with their phase composition, fiber-matrix interface and porosities. Preform P1 has low pyrolytic carbon content and large porosities. The alloyed melts can easily infiltrate into the pores in both the inter-fiber bundles and intra-fiber bundles during RMI production of the C/C-SiC composites. Due to the low carbon content and large

amount of infiltrated melts, some carbon fibers react with the infiltrated alloyed melt, which has a great negative effect on the mechanical strength of the C/C-SiC composite. On one hand, the reinforced effect of carbon fibers is reduced. On the other hand, the reaction results in a strong interface bonding and jeopardizes the flexural strength of the composites. Reaction of the infiltrated alloyed melts with carbon is time-dependent. Thus, flexural strength of the composite prepared using preform P1 decreases with an increase in the infiltration time.

Compared with preform P1, P2 has much larger pyrolytic carbon content. The pores in P2 are much smaller and less than that in P1. The infiltration of alloyed melts into the pores of P2 is more difficult, which may result in relatively larger porosities of the C/C-SiC composites. The open porosities of the C/C-SiC composites prepared by P1 and P2 for different infiltration time were measured and shown in table 2. As can be seen, the porosities of the C/C-SiC composites by P2 are generally larger than those by P1. For the C/C-SiC composites prepared by P2, the composite for 2h has the lowest porosity (3.3%), which attributes to the highest flexural strength of the resulting composite. The preform P2 may not be effectively infiltrated by the alloyed melts for 1 h and thus, the resulting C/C-SiC composite has the largest porosity (7.2%) and accordingly lower flexural strength than that for 2h. Additionally, the composite prepared for 1h has larger residual pyrolytic carbon content than that for 2 h, which may also decrease the flexural strength of the resulting composite because the more pyrolytic carbon content in the composite could degrade the fiber strength due to the difference of thermal expansion between the fibers and pyrolytic carbon [15-17]. The

C/C-SiC composites prepared by P2 for 2-4 h have slightly increasing porosities (3.3-4.5%), indicating the preform has been effectively densified by the alloyed melts. However, the carbon fibers in the inter fiber bundles and on the edges of the fiber bundles may be reacted with the infiltrated melts for too much longer infiltration time. The damage of these fibers and the slightly increasing porosities of the composites result in the decrease of the flexural strength of the C/C-SiC composites with the increase of infiltration time.

Fig.9

SEM photographs of the composites' fracture surfaces are shown in Fig.9. Fracture surface of the composite prepared using preform P1 is quite even without obvious pulling out of carbon fibers, which demonstrates a brittle fracture behavior. During reactive melt infiltration of preform P1, the alloyed melt infiltrates into both the intra-fiber bundles and the inter-fiber bundles. Some carbon fibers in the intra-fiber bundles react with the infiltrated melt (see Fig.6), which results in a strong interface bonding. The reaction-formed phases bond to the carbon fibers tightly and the cracks formed within the matrix cannot be stopped or deflected around the carbon fibers. Thus, the composite shows a brittle fracture behavior with a relatively flat fracture surface. However, preform P2 owns a high carbon content and low porosity. The pores in the intra-fiber bundles are mostly filled with pyrolytic carbon, which can protect the carbon fibers from being reacted. There is still a certain amount of residual

carbon in the resulting C/C-SiC composite, forming a weak fiber/matrix interface. Lots of carbon fibers split from the matrix and cracks formed in the matrix can deflect along the weak interfaces. Consequently, the C/C-SiC composite is toughened and shows a pseudo-ductile fracture behavior.

4. Conclusions

(1) C/C-SiC composites were prepared by reactive melt infiltration with Si-Zr10 alloyed infiltrant for different infiltration time.

(2) The composites prepared with C/C preform 1.38 g/cm^3 for 1 and 2 h are composed of C, SiC and ZrSi_2 phases while the composites prepared for 3 and 4 h are composed of C, SiC, ZrSi_2 and ZrC phases.

(3) The composites prepared with C/C preform 0.9 g/cm^3 for 1, 2 and 3 h are composed of C, Si, SiC and ZrSi_2 phases while the composite prepared for 4 h is composed of C, SiC and ZrC phases.

(4) Flexural strength of the composites prepared using preform 0.9 g/cm^3 decreases with the extension of infiltration time while that of the composites prepared using preform 1.38 g/cm^3 increase initially and then decreases reversely.

Acknowledgments

This work was supported by National Natural Science Foundation of China (51302315), Innovation Foundation for Excellent Postgraduate of National University of Defense Technology and Hunan Provincial Innovation Foundation for Postgraduate. Yonggang Tong also thanks the support from China Scholarship Council.

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Tables

Table 1 Density and volume fractions of carbon fiber, pyrolytic carbon and open porosity in C/C preforms.

C/C preform	Density (g/cm ³)	Carbon fiber (%)	Pyrolytic carbon (%)	Open porosity (%)
P1	0.90	29.0	18.6	49.4
P2	1.38	29.0	41.4	24.6

Table 2 Open porosities of the C/C-SiC composites prepared by preform P1 and P2 for different infiltration time.

Infiltration time (h)	C/C-SiC composite by P1 (%)	C/C-SiC composite by P2 (%)
1	2.8	7.2
2	2.1	3.3
3	2.4	3.8
4	2.5	4.5

Figure captions:

Fig.1 XRD patterns of the C/C-SiC composite prepared for different infiltration time with a C/C preform of 1.38 g/cm³.

Fig.2 XRD patterns of the C/C-SiC composite prepared for different infiltration time with a C/C preform of 0.9 g/cm³.

Fig.3 Phase diagram of Zr-Si-C system at 1200 °C [14].

Fig.4 Changes in Gibbs free energy as a function of temperature for Reaction (1).

Fig.5 Cross-section SEM micrographs of C/C-SiC composites prepared for different infiltration time with C/C preform of 0.9 g/cm³ (a, b) 1h; (c, d) 2h; (e, f) 3h; (g, h) 4 h.

Fig.6 Some siliconized carbon fibers in the intra fiber bundles of C/C-SiC composites prepared in 3h with C/C preform 0.9 g/cm³.

Fig.7 Cross-section SEM micrographs of C/C-SiC composite prepared in 2h with C/C preform 1.38 g/cm³.

Fig.8 Flexural strength of C/C-SiC composites prepared in different infiltration time.

Fig.9 SEM photographs of the fracture surfaces of C/C-SiC composites prepared using (a, b) preform 0.9g/cm³ with infiltration time in 1h and (c, d) preform 1.38 g/cm³ with infiltration time in 3 h.