

Reaction diffusion in continuous SiC fiber reinforced Ti matrix composite

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Abstract: SiC continuous fiber-reinforced pure Ti(TA1) matrix composites were fabricated by a vacuum hot pressing(VHP) method and then heat-treated in vacuum under different conditions. The interfacial reaction and the formation of interfacial phases were studied by using SEM, EDS and XRD. The results show that there exists reaction diffusion at the interface of SiC fibers and Ti matrix, and the concentration fluctuation of reaction elements such as C, Ti and Si appears in interfacial reaction layer. The interfacial reaction products are identified as Ti_3SiC_2 , TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$. At the beginning of interfacial reaction, the interfacial reaction products are TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$. Along with the interfacial reaction diffusion, Ti_3SiC_2 and $\text{Ti}_5\text{Si}_3\text{C}_x$ single-phase zones come forth in turn adjacent to SiC fibers, and the $\text{TiC}+\text{Ti}_5\text{Si}_3\text{C}_x$ double-phase zone appears adjacent to Ti matrix, which forms discontinuous concentric rings by turns around the fibers. The formed interfacial phases are to be Ti_3SiC_2 , $\text{Ti}_5\text{Si}_3\text{C}_x$ and $\text{TiC}_x+\text{Ti}_5\text{Si}_3\text{C}_x$ from SiC fiber to Ti matrix. The interfacial reaction layer growth is controlled by diffusion and follows a role of parabolic rate, and the activation energy (Q^k) and (k_0) of SiC/TA1 are 252.163 kJ/mol and $7.34 \times 10^{-3} \text{ m/s}^{1/2}$, respectively.

Key words: SiC/TA1 composite; reaction diffusion; interfacial phases; activation energy

1 Introduction

Due to their high specific strength and specific modulus, SiC fiber reinforced Ti alloy-matrix composites (TMCs) can be used for aero-engines[1]. The interfacial reaction taking place during the composite consolidation and high temperature service lead to the formation of some brittle compounds distributed in several layers at the interface. The brittle interfacial reaction products become the crack origination that makes the interface lose its stability and the ability of transferring the applied load[2].

Numerous studies have tried to analyze the interfacial reaction diffusion in Ti matrix composites reinforced with SiC continuous fiber[3–7]. The emphases are usually focused on the reaction thermodynamics between the matrix and the reinforcement, the growth dynamics of interfacial reaction product layer, the diffusion barrier coatings as well as the reaction product layers that prevent the

diffusion of Ti, Si and C elements. Due to the different types of SiC fiber and Ti alloy matrix, there are many controversies in the formation types and formation sequence of the interfacial reaction products. For example, the interfacial reaction products from fiber to matrix are usually Ti_3SiC_2 , $\text{Ti}_5\text{Si}_3\text{C}_x$, TiC_x and Ti_3Si for the SiC fiber without C coating[8–9]. For the SiC continuous fiber containing C-coating, before the C-coating is consumed completely, the interfacial reaction product is only TiC_x [10]. For the SiC fiber coated by a C-rich layer containing SiC particles, such as SCS-6 SiC fiber, the interfacial reaction products are identified as TiC_x , $\text{Ti}_5\text{Si}_3\text{C}_x$, TiC_x and Ti_3Si from the fiber to matrix[3,11]. For the selection of Ti alloy matrix, theoretically, all α , $\alpha+\beta$ and β Ti alloys can be considered the matrix materials. But when considering the fabricating technology and machining capability, $\alpha+\beta$ and β Ti alloys are usually chosen, i.e., Ti15V3Cr and Ti6Al4V. In addition, some Ti-Al intermetallic compounds such as Ti_3Al and Ti_2AlNb , having not only the oxidation resistance at high temperature, but also the

ability of being rolled into foil, can be selected as matrix materials. Due to the different reaction intensity degrees between SiC fiber and the matrix, the interfacial reaction and the formation of interfacial products are different from each other.

In order to study the interfacial reaction as well as the formation of the interfacial reaction products between SiC fiber and Ti matrix, industrial pure Ti was used as the matrix, which was reinforced by SiC continuous fiber with no C-coating. The composite was fabricated and heat treated under different conditions, and the morphology and elemental distributions as well as components of interfacial reaction zone were analyzed with the SEM, EDS and XRD methods. The aim of the investigation is to forecast the formation of interfacial reaction products in SiC/Ti composite and the diffusion path of reactive elements, as well as to provide the basis for studying the interfacial reaction in Ti alloys and Ti-Al intermetallic compounds matrix composites reinforced with SiC continuous fiber.

2 Experimental

Continuous β -SiC fibers with no C-coating produced by a chemical vapour deposition(CVD) process were used as reinforcements. The fiber was about 100 μm in diameter. The matrix material used for this experiment was industrial pure Ti (named TA1) foils with a thickness of about 50 μm . Unidirectionally aligned composites of TA1 reinforced with SiC fibers were fabricated by solid-state foil-fiber-foil consolidation technique using a vacuum hot pressing(VHP) process to full density. The VHP process was done at 850 $^{\circ}\text{C}$ under a pressure of 50 MPa for 40 min. After its fabrication, the composites were heat-treated in vacuum at 800, 900 and 1 000 $^{\circ}\text{C}$, respectively.

Samples were cut from composites perpendicular to the fiber direction with a low-speed diamond saw. The cross section was prepared by grinding step by step with 400, 600, 1 000 and 1 200 grit silicon carbide metallographic papers, polishing with 1 μm diamond paste, then etching for about 2 s with a solution made of 1 mL HF, 3 mL HNO_3 and 7 mL H_2O , and cleaning with water immediately. After sipping up water with filter paper, the samples were immersed in acetone or absolute alcohol for 3–5 min to get rid of water. Finally the dehydrated samples were dried by hot air, encased with qualitative filter paper and put into an airtight container for use later.

The morphologies of interfacial reaction products were examined with JSM 6460 scanning electron microscopy(SEM). The phases in the composites were identified by X-ray micro-area diffraction(XRD) equipped with Panalytical X'Pert PRO and the diameter

of the micro-area was 100 μm . The elements' contents were analysed with Oxford INCA7574 energy dispersive spectrometer(EDS).

3 Results and discussion

3.1 Interfacial reaction of SiC/TA1

Figs.1–3 show the interfacial reaction zone morphologies of SiC/TA1. During the course of heat-treatment of the composites, the interfacial reaction zone becomes thicker and thicker along with prolonged time and enhanced temperature. At the same time, the interfacial reaction products tend to form discontinuously concentric rings around the fiber, which can be observed

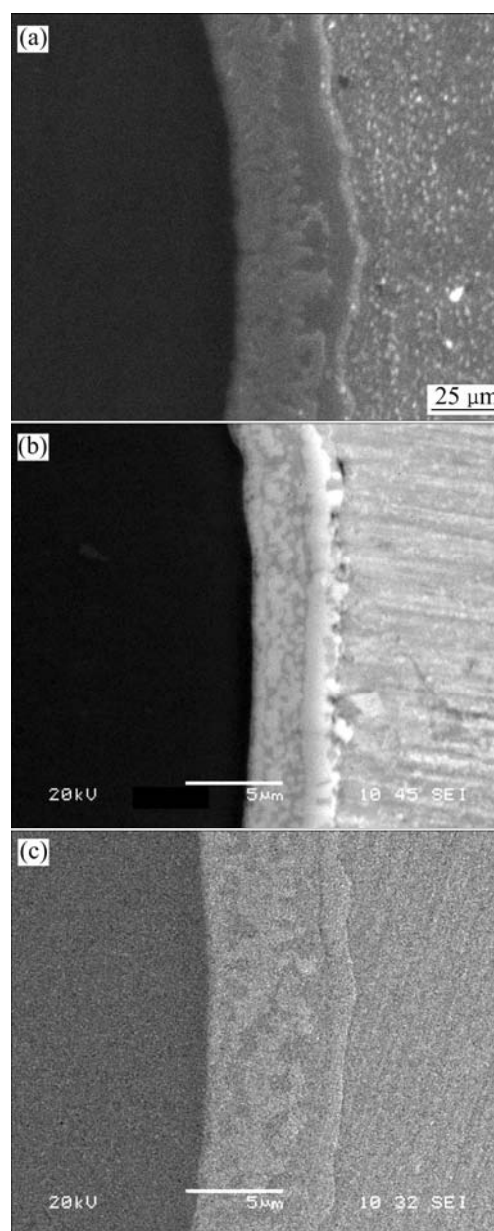


Fig.1 SEM micrographs of interfacial reaction zone of SiC/TA1 composite: (a) 800 $^{\circ}\text{C}$ for 94 h; (b) 800 $^{\circ}\text{C}$ for 206 h; (c) 800 $^{\circ}\text{C}$ for 500 h

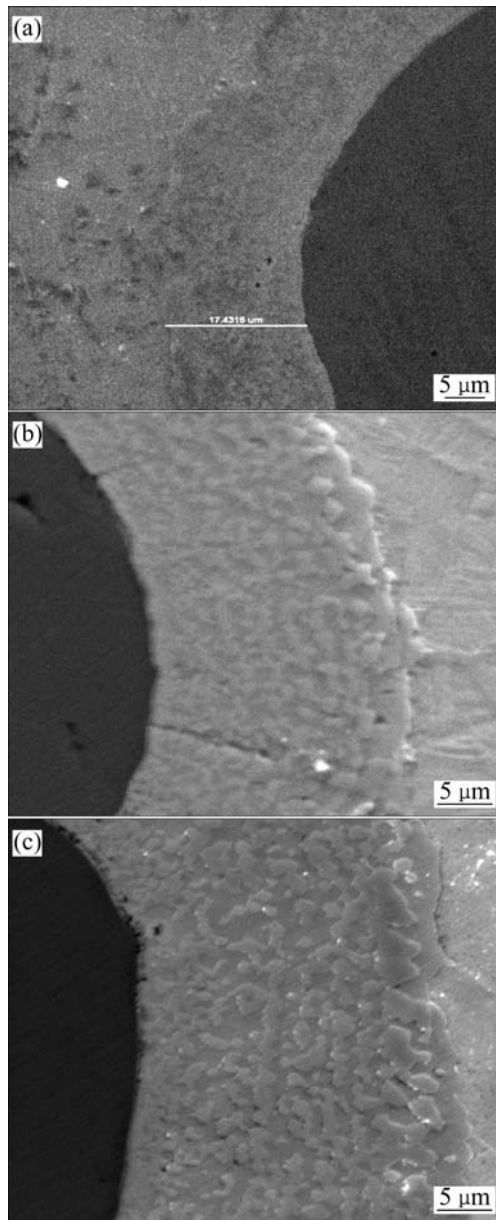


Fig.2 SEM micrographs of interfacial reaction zone of SiC/TA1 composite: (a) 900 °C for 73 h; (b) 900 °C for 150 h; (c) 900 °C for 240 h

clearly in Figs.2 and 3. Fig.4 shows the EDS surface analysis result of interfacial reaction zone, and it can be found the interfacial reaction layers are formed by turns with carbide and silicide of titanium.

Figs.5–7 are EDS line and point analysis results of interfacial reaction zone. Seen from the figures, the concentration fluctuation of reactive elements such as C, Ti and Si appears in interfacial reaction layers, which indicates that the Si and C atoms diffuse from SiC fiber to the matrix, and the Ti atoms diffuse in the opposite direction. From EDS line analysis result as well as Tables 1 and 2, the interfacial reaction zone is mostly $TiC_x + Ti_5Si_3C_x$ duplex phase zone, and the ternary phase

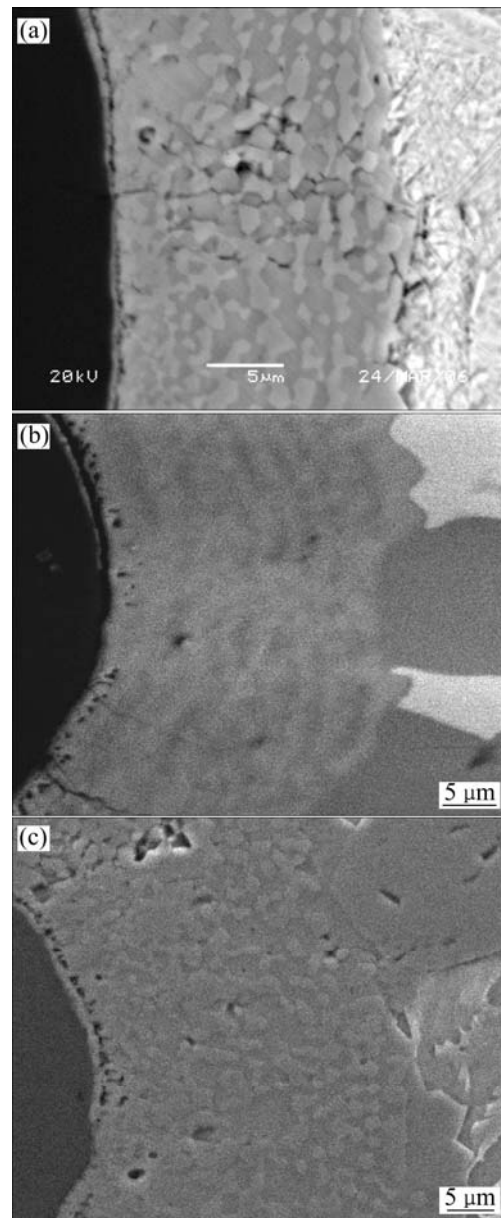


Fig.3 SEM micrographs of interfacial reaction zone of SiC/TA1 composite: (a) 1 000 °C for 40 h; (b) 1 000 °C for 91 h; (c) 1 000 °C for 260 h

Table 1 EDS point analysis results of interfacial reaction layers of SiC/TA1 (mole fraction, %)

Point*	C	Si	Ti
1	50.89	49.11	—
2	32.23	30.49	37.29
3	26.53	32.38	41.09
4	44.89	3.65	51.46
5	23.41	33.92	42.67
6	25.34	32.85	41.81
7	44.86	—	55.14
8	19.13	24.76	56.11

* Position of analysis points can be seen in Fig.6

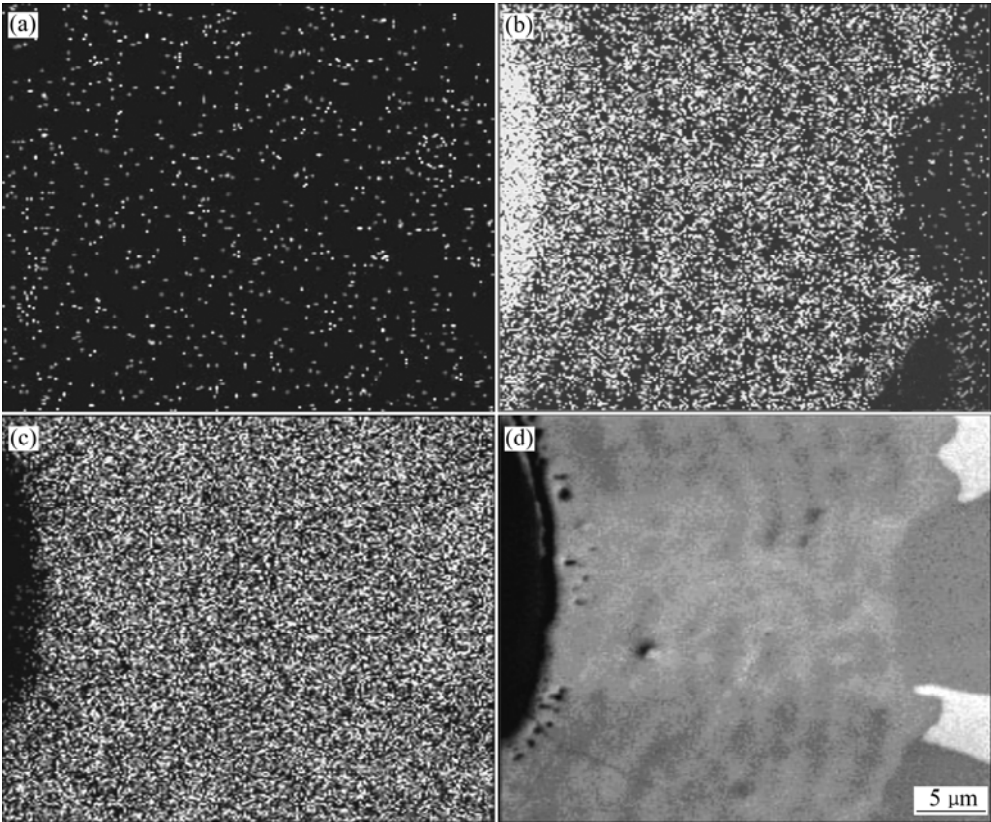


Fig.4 EDS surface analysis results of interfacial reaction zone (1 000 °C for 91 h): (a) C; (b) Si; (c) Ti; (d) Grey image

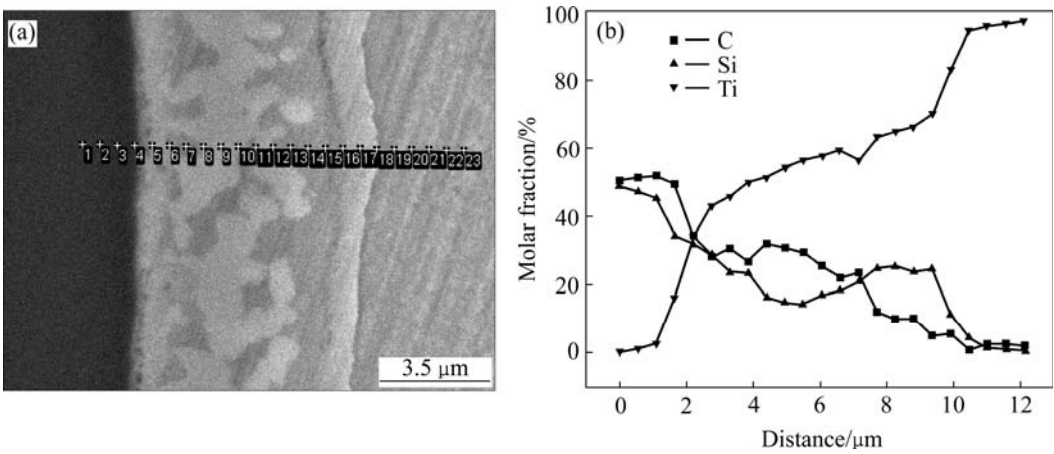


Fig.5 Position and EDS line analysis result of interfacial reaction zone (800 °C for 500 h): (a) SEM micrograph; (b) Linear analysis

Table 2 EDS point analysis results of interfacial reaction layers of SiC/TA1(molar fraction, %)

Point*	C	Si	Ti
1	44.23	55.77	—
2	15.62	20.12	64.26
3	9.86	30.45	59.69
4	35.46	4.00	60.54
5	35.20	4.22	60.58
6	7.38	26.55	66.07
7	6.08	29.20	64.72
8	39.01	—	60.99
9	7.62	—	92.38

* Position of analysis points can be seen in Fig.7

Ti₃SiC₂ may come into being adjacent to SiC fiber. As soon as the annealing time is long enough, the interfacial reaction layer is thick enough, and the Ti₅Si₃C_x single phase zone appears between the ternary Ti₃SiC₂ and Ti₅Si₃C_x+TiC_x duplex phase zone.

Figs.8–10 show the X-ray micro-area diffraction patterns of the interfacial reaction zone, and it indicates obviously that in all cases the interface phases existing in the composites contain TiC_x and Ti₅Si₃C_x. Along with the enhanced annealing temperature and time, the diffraction intensity of Ti₃SiC₂ becomes more and more obvious. When it is heat treated at lower temperature, the diffraction peak is very tiny, or even does not appear.

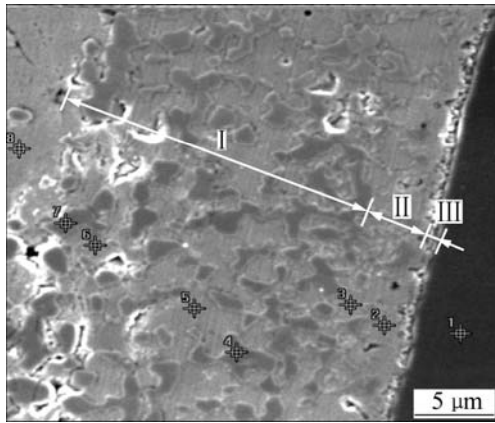


Fig.6 Position and EDS point analysis result of interfacial reaction zone (900 °C for 240 h): I $\text{Ti}_5\text{Si}_3\text{C}_x+\text{TiC}_x$; II $\text{Ti}_5\text{Si}_3\text{C}_x$; III Ti_3SiC_2

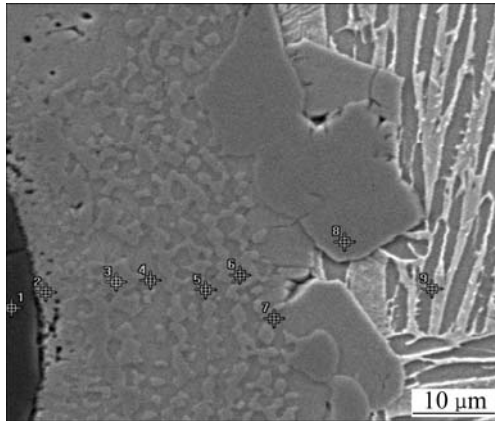


Fig.7 Position and EDS point analysis result of interfacial reaction zone (1000 °C for 260 h)

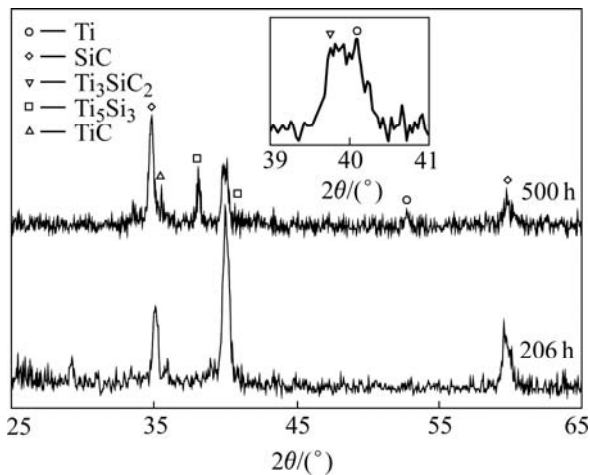


Fig.8 X-ray micro-area diffraction patterns of SiC/TA1 after heat treatment at 800 °C

As shown in Fig.8, when SiC/TA1 composite is heat treated at 800 °C for 206 h, there is no Ti_3SiC_2 diffraction peak.

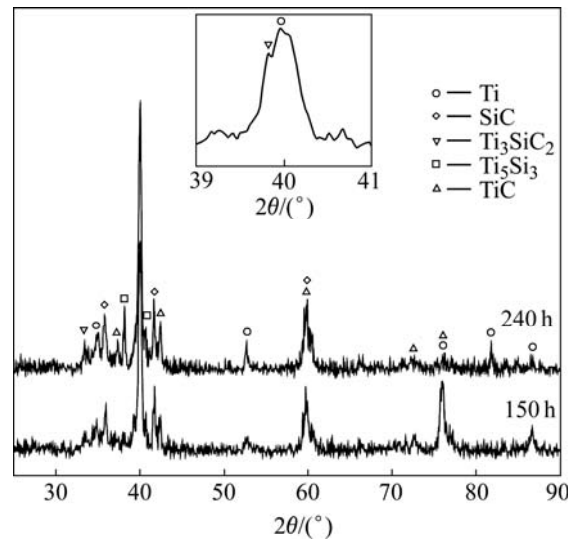


Fig.9 X-ray micro-area diffraction patterns of SiC/TA1 after heat treatment at 900 °C

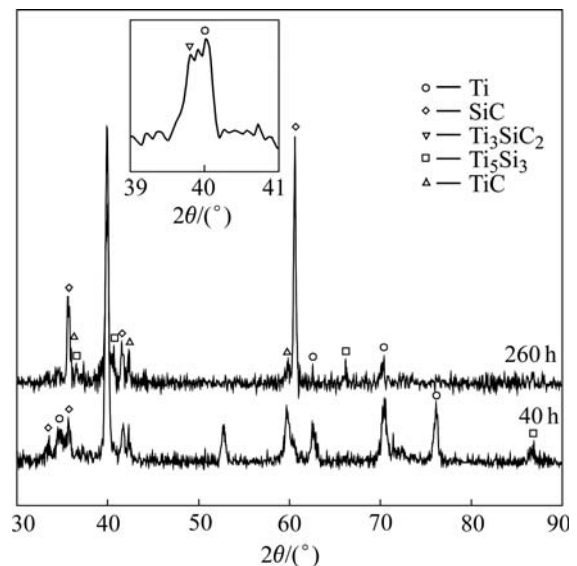


Fig.10 X-ray micro-area diffraction patterns of SiC/TA1 after heat treatment at 1000 °C

3.2 Formation of interface phase

The thermochemical compatibility of fiber/matrix interface is of primary concern in SiC continuous fiber-reinforced Ti matrix composites. Interface stability in multi-component system is controlled by a number of chemical, thermodynamic and kinetic factors[12]. The interfacial reaction products of SiC/TA1 were identified as Ti_3SiC_2 , TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$, and C atoms may carry on long distance diffusion to react with the matrix or form interstitial solid solution[13]. Reaction of C and Si with Ti matrix is thermodynamically favored under the present consolidation and heat-treatment conditions:





For SiC/TA1 composite the free energy change of the four reactions above are about -170 , $-1\,356$, -895.4 , -578.5 kJ/mol at $1\,000$ K [14], respectively. Hence, from the point of view of thermodynamics, the reactions are spontaneous between the SiC fibers and the matrix during the consolidation and the heat treatment of the composites.

Fig.11 shows the schematic representation of interface reaction products formation of SiC/TA1 composite. Generally, the interfacial reaction is a reaction-controlled process in its very early stage, and the interfacial products are $\text{Ti}_5\text{Si}_3\text{C}_x$ and TiC_x according to Eqn.(3), TiC_x is adjacent to Ti side, while $\text{Ti}_5\text{Si}_3\text{C}_x$ is adjacent to SiC side, respectively [15]. As long as the interfacial reaction layer becomes thicker, its growth is controlled by diffusion, and Ti, Si and C atoms inter-diffuse through interfacial reaction layer. Since the initial TiC_x isn't continuous, the inner $\text{Ti}_5\text{Si}_3\text{C}_x$ and the outer TiC_x contact with Ti matrix simultaneously. That is, the diffusion from SiC fiber to Ti matrix may through $\text{Ti}_5\text{Si}_3\text{C}_x$ and TiC_x , or only through $\text{Ti}_5\text{Si}_3\text{C}_x$. At the same time, the diffusion coefficient of Ti atoms is much less than that of C and Si atoms [16–17]. Consequently, the advanced speed of the reaction layer/matrix interface may be controlled by the diffusion of Ti atoms. Only a few of Ti atoms diffusing out can the zone in front of reaction layer/matrix be come to the concentration points of $\text{Ti}_5\text{Si}_3\text{C}_x$ and TiC_x in Ti-Si-C ternary phase diagram. Therefore, as soon as the concentration in front of the $\text{Ti}_5\text{Si}_3\text{C}_x/\text{Ti}$ interface comes to that of TiC_x , then TiC_x

forms subsequently. In the same way, when the concentration in front of the TiC_x/Ti interface comes to that of $\text{Ti}_5\text{Si}_3\text{C}_x$, then $\text{Ti}_5\text{Si}_3\text{C}_x$ forms. Thus the interfacial reaction products layer appears to be discontinuously concentric rings around the fibers. Along with the diffusion of C and Si atoms and the $\text{Ti}_5\text{Si}_3\text{C}_x$ layer becoming even thicker, there are no more Ti atoms arriving at SiC/ $\text{Ti}_5\text{Si}_3\text{C}_x$ interface, but excessive C atoms pile up there, so as to form the ternary phase, Ti_3SiC_2 . In addition, C atoms may carry on long distance diffusion to react with the matrix and form TiC in matrix. The formed interfacial phases are SiC, Ti_3SiC_2 , $\text{Ti}_5\text{Si}_3\text{C}_x$, $\text{TiC}_x + \text{Ti}_5\text{Si}_3\text{C}_x$ and Ti from SiC fiber to Ti matrix.

3.3 Growth kinetics of interfacial reaction products of SiC/TA1 composite

From Figs.1–3, it can be seen that the thickness of the reaction layer becomes thicker and thicker along with the enhanced heat-treated temperature and prolonged heat-treated time. The measured thickness of the interfacial reaction layer in SiC/TA1 composite is summarized in Table 3. The temperature is more effective than the time in the reaction layer growth, for example, the reaction layer thickness of $17.3\ \mu\text{m}$ is measured in SiC/TA1 heat-treated at $1\,000\ ^\circ\text{C}$ for 40 h, but it is only $7.55\ \mu\text{m}$ at $800\ ^\circ\text{C}$ even for 500 h.

As mentioned above, the interfacial reaction is reaction-controlled in the early stage but soon becomes diffusion-controlled when a thin reaction layer forms. A diffusion-controlled growth may be satisfied with a parabolic law [8,13]:

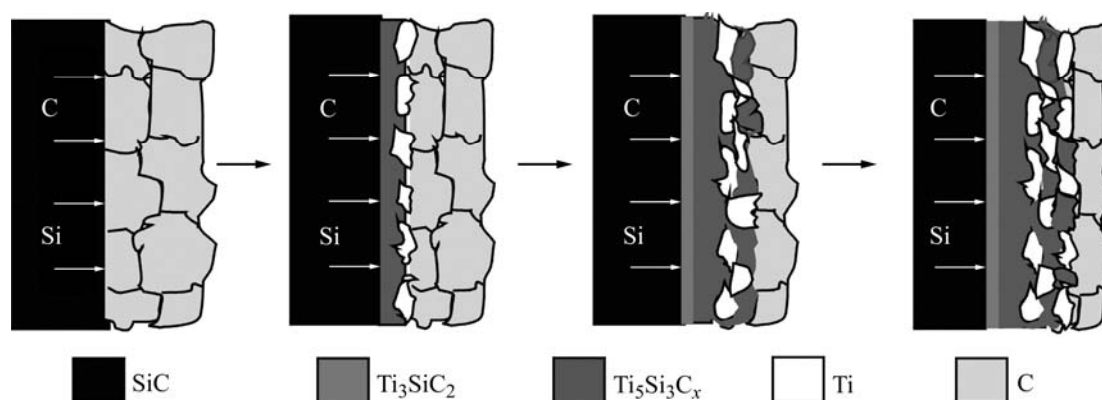


Fig.11 Schematic representation of interface reaction product formation of SiC/TA1 composite (Arrows show diffusion way of C and Si)

Table 3 Thickness of interfacial reaction layer (μm)

As-processed	800 $^\circ\text{C}$			900 $^\circ\text{C}$			1 000 $^\circ\text{C}$		
	94 h	206 h	501 h	73 h	150 h	240 h	40h	91 h	260 h
1.2	4.33	5.31	7.55	17.1	23.1	28.2	17.3	27	40.2

$$l=kt^{1/2}+b_0 \quad (5)$$

where l is the thickness of the interfacial reaction layer, k is a rate constant which is related to the diffusion coefficient of the components and to the thermodynamic properties of the interfacial reaction products, t is time and b_0 is the original thickness of the reaction layer in the as-processed samples.

Fig.12 shows the relationship between the thickness of the reaction layer and the square root of the reaction time at different temperatures for SiC/TA1 composites.

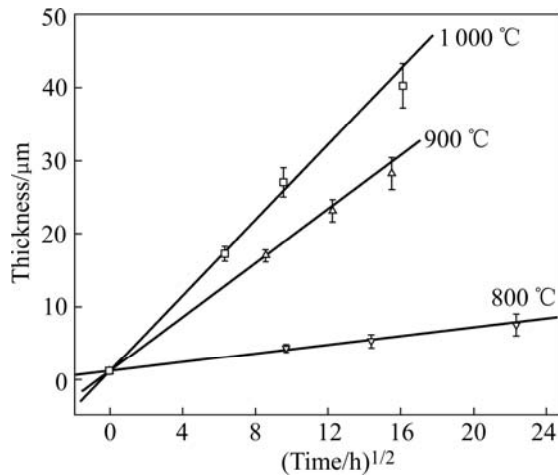


Fig.12 Interfacial reaction kinetic curves of SiC/TA1

The data points for each treatment temperature are fitted with a straight line to estimate a generalized reaction rate constant. The fitted equations are

$$l=0.281 \ 6t^{1/2}+1.331 \ 39 \quad (800 \text{ } ^\circ\text{C}) \quad (6)$$

$$l=1.070 \ 103t^{1/2}+1.695 \ 18 \quad (900 \text{ } ^\circ\text{C}) \quad (7)$$

$$l=2.474 \ 08t^{1/2}+2.389 \ 47 \quad (1 \ 000 \text{ } ^\circ\text{C}) \quad (8)$$

The thickness l is in μm , and time t is in hour for the three equations.

These equations provide quantitative descriptions for the interfacial reactions of the composites, from which the reaction results at a specific time and temperature can be calculated. Furthermore, the fact that the k value increases with the increase of the reaction temperature reveals the importance of fabricating these composites at a lower temperature.

In addition the rate constant k in Eqn.(5) follows Arrhenius relation[8]:

$$k=k_0\exp(-Q^k/2RT) \quad (9)$$

where k_0 is the pre-exponential factor, which is also related to the diffusion coefficient and to the thermodynamic properties, Q^k is the growth activation energy, R is the gas constant ($R=8.346 \ 2 \text{ J/K}$), and T is the temperature.

Fig.13 shows the Arrhenius plot of the parabolic rate constant of SiC/TA1. The values k_0 and Q^k calculated according to Eqn.(6) are 252.163 kJ/mol , $7.34 \times 10^{-3} \text{ m}\cdot\text{s}^{-1/2}$, respectively. The values are well fitted with those calculated by MARTINEAU[8].

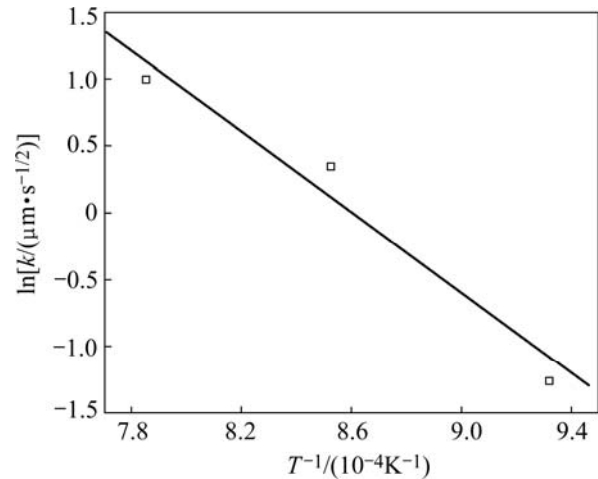


Fig.13 Arrhenius plot for parabola rate constant of SiC/TA1 composites

4 Conclusions

1) The interfacial reaction takes place between SiC reinforcement and Ti matrix, and the interfacial reaction products are identified as Ti_3SiC_2 , TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$.

2) At the beginning of interfacial reaction, the interfacial reaction products are TiC_x and $\text{Ti}_5\text{Si}_3\text{C}_x$, in which TiC_x is discontinuous. Along with the enhanced heat-treatment temperature and prolonged heat-treatment time, Ti_5Si_3 forms in front of the TiC_x/Ti interface, and TiC_x forms in front of the $\text{Ti}_5\text{Si}_3\text{C}_x/\text{Ti}$ interface, thus the interfacial reaction product layer presents the discontinuously concentric rings around the fibers. At the same time, the ternary phase, Ti_3SiC_2 , may come into being between SiC fiber and the reaction products.

3) The interfacial reaction layer growth is controlled by diffusion and follows a role of parabolic rate, and the activation energy Q^k and k_0 of SiC/TA1 are 252.163 kJ/mol and $7.34 \times 10^{-3} \text{ m}\cdot\text{s}^{-1/2}$, respectively.

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