Rare Metal Materials and Engineering
Volume 38, Issue 2, February 2009
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2009, 38(2): 0209–0213.

ARTICLE

Ti Metallization of C_f/SiC Composites Surface by Molten Salt Reaction

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Abstract: Ti metallized coating was prepared on the surface of carbon fiber reinforced silicon carbide matrix (C_f/SiC) composite by molten salt reaction to make joining the composite with high melt point metals such as Ti. The morphologies and compositions of Ti metallized coating were analyzed by SEM and EDS. The phase components were assessed by XRD. The wettability of the solder was measured by quantitative metallography. The results show that Ti metallized coating is uniform and dense, and bound with the matrix closely. Ti can infiltrate into the gaps of the fibers, and cover the surfaces of the C_f/SiC composite. The main phases of the metalized coating consist of TiC and Ti_5Si_3. There are three transition layers between SiC and the metallized, i. e. Ti_5Si_3 layer, TiC layer and Ti_5Si_3 layer. The wettability of C_f/SiC composites surface to Ti is greatly improved by metallization, and the contact angle is deceased from 153.9° to 13.2° at 950 °C.

Key words: C_f/SiC composites; molten salt; titanium metallization; wetting angle

Owing to its low density, excellent mechanical properties and high fracture toughness at elevated temperatures, carbon fiber reinforced silicon carbide matrix (C_f/SiC) composite find the potential applications at high temperatures, as structural materials, in different fields including advanced engines, gas turbines for power/steam co-generation, heat exchangers, heat treatment and materials growth furnaces, as well as nuclear reactors of the future[1]. However, in most areas mentioned above, metal is still the main raw material. To be put into practice, reliable joining of C_f/SiC composite with refractory metals (such as Ti and Nb) is required. Mechanical joining with a complex joint provides low airtightness and increases the weight and size of components. The thermal stress of bolt joining is great, which hurts C_f/SiC composite. Brazing and diffusion bonding are reasonable choices. Three problems should be dissolved to join ceramic matrix composite and refractory metals effectively. The first is the poor wettability between brazing alloy and composite, which make it difficult for the brazing alloy to spread on the surface of the composite. The second is the obvious difference of thermal expansion coefficient between the composite and refractory metal (C_f/SiC: 1-3×10^{-6}/K; Ti: 7-8×10^{-6}/K). Transition layer with proper thermal expansion coefficient is necessary. The third is the weak bond between the brazing alloy and the composite. Therefore, the joining with high intensity is difficult to be obtained. Metallized coating on C_f/SiC composite before brazing can resolve all the three problems. Accordingly, this is a reasonable measure to get an excellent joint.

The main methods to prepare metallized coating on ceramic include Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD) and thermal spraying etc. PVD is a high costly and complex process, and the joining strength between coating and matrix is low. The coating made by thermal spraying is not even and the thickness is difficult to be controlled. Therefore, a simple low-cost method to prepare a dense, homogenous and high performance coating is important for the joining of C_f/SiC composite and metal. Pan Wei, Huang Qiliang etc.[2-5] used molten salt method to prepare Ti metallized coating on aluminium nitride. The metallized coating was formed by the interface reaction of Ti and AlN. The carbon and silicon had good appetency with Ti. During the molten salt reaction, TiC and Ti_5Si_3 were formed on the sur-

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face of the composite to construct the metallized coating. The thermal expansion coefficients of TiC and Ti_5Si_3 were between that of C_f/SiC composite and Ti. The wetability between the brazing alloy and the metallized coating could be improved greatly. Furthermore, the performances of joints were improved.

In this paper, molten salt reaction was firstly adopted to prepare Ti metallized coating on C_f/SiC composite. The phase compositions and the microstructure of the metallized coating were characterized and the wettability of the brazing alloy and the metallized coating was tested.

1 Experimental procedure

The experiment was carried out in the furnace designed by ourselves. C_f/SiC composite used in this work was fabricated by precursor infiltration and pyrolysis (PIP) in State Key Laboratory of Advanced Ceramic Fibers & Composites in China. After polished by diamond lapping paste, the samples were cleaned in water and ethanol.

Equal moles of NaCl-KCl and K_2TiF_6 were mixed together. The C_f/SiC composite and titanium powder were put into the mixed salt, and then placed into an alumina crucible with high purity. The assembly was heated to a designed temperature for certain time in Ar atmosphere. After cooled to room temperature, the composite samples were taken out from the assembly.

The microstructure of the metallized coating was characterized by KH-3000 three directional microscope and Sirion200 scanning electron microscopy (SEM). The elements of the metalized coating were analyzed by EDAX accessories. The phase compositions of the coating were assessed by D8 Advance X-ray diffraction (XRD).

Wettability was characterized by the change of the spraying areas and wetting angle of the brazing alloy before and after brazing. The brazing alloy（Ti-Cu-Zr-Ni） foil with 3 mm×6 mm×0.3 mm was used. After cleaned in ethanol, the foil was dried and put on the join face of the uncoated and coated samples. Brazing was carried out at 950 ^{o}C for 10 minutes and the heating rate was 10 ^{o}C/min, at the pressure of 2.7×10^{-3}Pa. wetting angle was tested by KH-3000 three directional microscope and the spraying area was tested by quantitative metallography.

2 Results and discussion

2.1 Microstructure of metallized coating on the C_f/SiC composite

Fig.1 shows the cross-sectional feature of the unmetallized C_f/SiO_2 composite with different magnifications. The carbon fibers in a fiber bundle as a unit were woven in three dimension way during processing of C_f/SiC composite. Silicon carbide was filled in the gap between fibers and bundles, and was coated on the surface of the composite. There were a lot of pores in the gap of fibers and fiber bundles because of the PIP process. If the surfaces of the above mentioned fibers and bundles were used to be joined, the brazing alloy could not infiltrate the gaps easily owing to the great surface tension, and the effective joint area was small. Meanwhile, the shear strength of the carbon fiber in vertical direction is low, and the carbon fibers were easy to be broken under shear force, resulting in low join intensity.

Fig. 2a, b and c show the microstructures of boundary of SiC and carbon bundles of the coated C_f/SiC composite. All the surfaces of the samples were covered by metallized coating. The naked carbon fibers were also covered completely. Owing to the fact that the activenesses of SiC, carbon fibers and titanium are different, the surface microstructures of different areas are distinct. On the SiC area, titanium crystals were deposited in the mode of layer growth. The crystals had uniform sizes and were arrayed tightly. On the area of carbon bundles, titanium reacted with carbon to form fine TiC crystals. Fig. 2d is the microstructure of metalized coating on single carbon fiber. This fiber was covered by coating completely, and the coating sealed the pores effectively. As a result, the join area was increased, and the join intensity was enhanced. Fig. 2e shows the microstructure of metalized coating formed by two times of molten salt reaction. It can be seen from the microstructure of cross-section that the coating on the sample was even in thickness and bonded tightly with the composite. The average thickness of coating after first time of molten salt reaction was 10 μm. The second reaction could enhance the coating area and seal cracks, while the thickness was 20 μm.

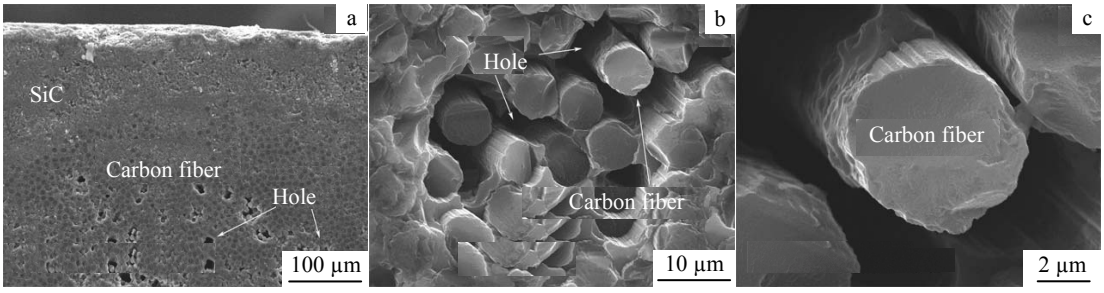

Fig.1 The cross-sectional feature of the C_f/SiC ceramic sample

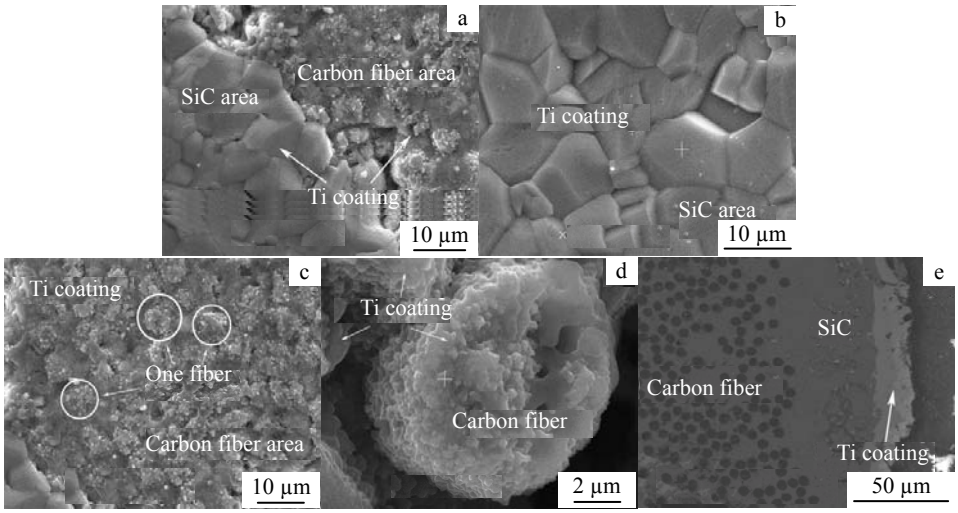

Fig.2 The surface and cross-sectional feature of the titanium layer deposited on the C_f/SiC ceramic sample: (a)(b)(c) coating on C_f/SiC; (d) coating on single carbon fiber; and (e) coating by two times molten salt reaction

Table 1 lists the EDS results of the coating on SiC area and carbon fiber area. The content of carbon in the coating on carbon fiber area was four times of that on SiC area. The different carbon contents caused the difference of coatings on two areas. In spite of the great difference of microstructures, the main element in metalized coating was still titanium which made the coating metallized.

2.2 Phase composition of the metallized coating

Fig. 3a is the XRD pattern of the uncoated C_f/SiC sample. The main phase of the sample was SiC. Carbon was not detected because carbon in the fibers was amorphous[6]. Fig 3b is XRD pattern of the coated sample. The main phases of the metalized coating consisted of TiC and Ti_5Si_3. There was weak SiC peaks in this pattern. The surface of the sample was completely covered by the coating and there was only little naked SiC.

Fig. 4 shows the SEM morphology and the element distribution of the interface of coating and SiC area of C_f/SiC composite. The researches on the interface reaction of Ti and SiC were carried out in the past time, most of which were focused on the reaction of SiC fiber reinforced titanium alloy at designed temperature but the surface reaction and its resultants were not identified yet[7-10]. It was found in the present research that there appeared two main resultants and three transition layers between SiC and metallized coating. The resultants were TiC and Ti_5Si_3. From the composite to the surface of the coating, the changes of elements were different. The content of titanium increased from SiC layer to the coating and achieved a higher value near the interface, which shows that titanium diffused into SiC in the reaction. The increase of Ti content appeared slowly in the coating. TiC was formed firstly because Ti has great binding force with C. The residual silicon atoms diffused into the Ti coating and were concentrated in the transition I. With the increase of reaction time,

Table 1 Chemical analysis of SiC area (the point in Fig.2b) and carbon fiber area (the point in Fig.2d) by EDAX

Element	SiC area (Fig.2b)wt%	Carbon fiber area (Fig.2d) wt%
C	05.28	22.51
Si	00.40	00.73
Ti	94.33	76.76

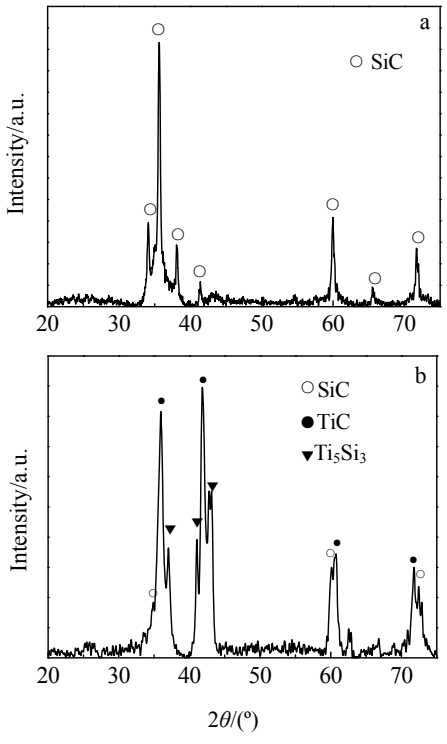

Fig.3 X-ray diffraction patterns of the original C_f/SiC (a) and titanium layer (b) deposited on the C_f/SiC ceramic sample

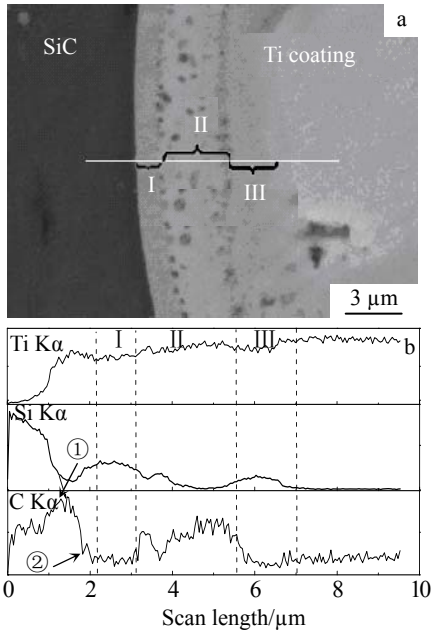

Fig.4 SEM micrographs (a) and EDS concentration profiles (b) of the interface between C_f/SiC and titanium layer

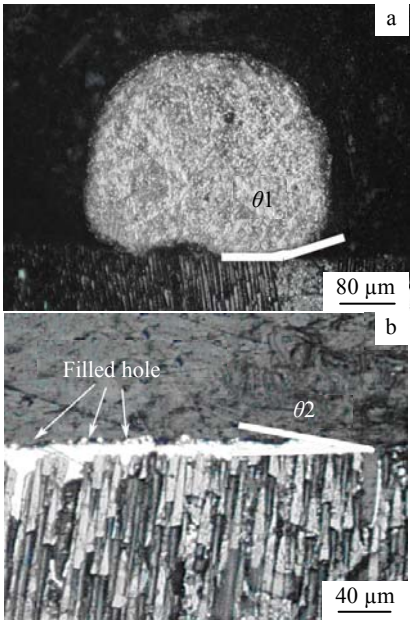

Fig.5 Wettability of solders on unmetalized C_f/SiC (a) and metalized C_f/SiC (b)

carbon in SiC would diffuse to the outer layer and the carbon in the interface diffused into the transition layer. The biggest content of carbon was in ① area and not in the interface. The deposited titanium had greater activity. While carbon diffused to the area, it would react with titanium. Hereby, carbon in the transition II was higher and the content of silicon was lower than that in transition I and transition III. According with the XRD pattern of coating, the main phase in transition I was Ti_5Si_3, and TiC in transition II, Ti_5Si_3 in transition III. The thermal expansion coefficients of TiC and Ti_5Si_3 were both between that of Ti and C_f/SiC composite. Then the coating would relax the thermal stress of joint. TiC and Ti_5Si_3 bound tightly with the composite and had good wettability with the brazing alloy, which enhanced the brazing intensity of the joint.

2.3 Wettability

Fig. 5 shows the micrographs of wettability of the samples. Fig. 5a shows the micrograph of the uncoated sample. The brazing alloy could not wet the C_f/SiC composite and displayed a ball shape. The wetting angle was 153.9°, and the wettability was bad. Fig. 5b shows the micrograph of the coated sample. The brazing alloy spread completely on the surface of C_f/SiC composite. Some brazing alloys flowed into the pores and sealed them. The wetting angle was decreased to 13.2°. Table 2 gives the spreading area and wetting angle of the brazing alloy on uncoated and coated samples at 950 °C. The spreading area on coated sample was 4.8 times of that on uncoated sample. The wettability of the brazing alloy on coated sample was much better than that on uncoated sample. The brazing alloy flowed into the pores, which would minimize the open porosity of the composite and increase the join area. The above mentioned will improve the joint intensity of C_f/SiC composite and refractory metal[11].

Table 2 Spreading area and wetting angle on original C_f/SiC and metalized C_f/SiC at 950 ℃

Material	Area of solder/mm^2	Spreading area/mm^2	Wetting angle/(°)
Original C_f/SiC	18	1.26	153.9
Metalized C_f/SiC	18	6.03	13.2

3 Conclusion

1) Titanium coating can be prepared on the surface of C_f/SiC composite by molten salt reaction. The metallized coating is dense and homogenous. The coating will seal the pores in the composite and cover both the SiC area and carbon fiber area completely.

2) The main composites of the metallized coating are TiC and Ti_5Si_3. The interfaces of SiC and metallized coating are Ti_5Si_3-TiC-Ti_5Si_3. The thermal expansion coefficient of the coating is between that of C_f/SiC composite and Ti, which reduce the thermal stress in the joint.

3) The brazing alloy can wet the coated C_f/SiC composite well, and increase the join area, which will improve the performance of the joint between C_f/SiC composite and the metal.

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熔盐法 C_f/SiC 复合材料表面钛金属化研究

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摘　要：为了实现 C_f/SiC 复合材料与难熔金属的连接，通过熔盐法在 C_f/SiC 复合材料表面沉积钛金属层。用 SEM 和 EDS 研究金属化层的形貌及成分；用 X 射线衍射分析金属化层的相组织；用定量金相法测量钎焊料的铺展特性。研究表明：钛金属化层均匀致密，与基体结合紧密，钛金属可渗入纤维间孔隙，比较完整地包覆在 C_f/SiC 复合材料外表面。金属化层主要成分为 TiC、Ti_5Si_3。金属化层与 SiC 界面分为 3 层，由内到外主要成分为 Ti_5Si_3、TiC 和 Ti_5Si_3。表面金属化后的 C_f/SiC 复合材料与钛合金钎焊料润湿性明显改善，润湿角从 153.9º降低为 13.2º。

关键词：C_f/SiC 复合材料；熔盐法；钛金属化；润湿角

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