# PREPARATION OF TI/AL/AL-CF MULTILAYER LAYERED COMPOSITES AND ITS INTERFACIAL REACTION

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**ABSTRACT**

In this work, we fabricated Ti/Al/Al-$C_f$ multilayered laminated composites by foil-fiber-foil (FFF) method. The results show that the Ti/Al/Al-$C_f$ multilayered laminated composites are successfully prepared by the hot pressing process. The temperature plays a leading role in the interfacial reaction, and the role of pressure is relative weak. From 660℃to 750℃,in general, the higher the temperature, corresponds with the stronger the interfacial reaction. However, the viscosity jump at 700℃, resulting in fluidity mutation, therefore, the pressure occupy a leading role. The thickness of the diffusion layer is about 8μm at the interface between Ti and Al where atoms diffuse mutually, and the main formation phase is $Al_3Ti$. At the interface of Al and C fiber, there is a concentration gradient of Al and C elements, and the thickness of the diffusion layer is about 2μm.The main reacting phase is $Al_4C_3$, when the C fiber is with nickel coatings,while the main reacting phase is $Al_3Ni$.

## 1. INTRODUCTION

With the development of science and technology, there is a higher demand for material performance, for single material has been difficult to meet the special or comprehensive required performance. On the one hand, it needs high strength low density, high temperature stability for the structural materials, on the other hand, it requires properties of functional materials, such as: heat, chemical, electrical, magnetic and other characteristics for application[1-3]. The metal matrix composites have high specific strength, specific stiffness, specific modulus, which has been widely used in automobile and aerospace fields[4]. Generally, the widely used metal matrix contains aluminum, magnesium and titanium alloy, etc. The Ti-based composites material has high strength, good rigidity, according the research ever reported[5-6]. In recent years, the study of the design, fabrication and properties of layered composites has attracted wide attention [7-10]. Material workers have put forward a lot of new ideas about the material system, material preparation and material properties [11]. In these researches, the biomimetic structure is designed based on the energy dissipation mechanism. This material can reduces the dependence of the mechanical properties on the original crack defects, which means it is a kind of defect-insensitive composite material.

The preparation process of C fiber reinforced metal matrix composites determines the performance of material. People have explored several fabrication method for continuous carbon fiber reinforced metal matrix composites, including vacuum pressure infiltration method, extrusion casting method, and

so on[12,13]. Among them, it's easy to control the volume fraction of the fiber by the foil-fiber-foil (FFF) method[14] compared with other preparation methods, therefore, it is a very promising to prepare the composite material with excellent properties by FFF method.

In this paper, Ti/Al/$C_f$ layered composites were prepared through foil-fiber-foil (FFF) method by vacuum hot pressing and sintering. With the advantages of low density and high strength, it was strengthened by C fiber and Ti/Al interfacial intermetallic compounds. Microstructural analysis was carried out by scanning electron microscopy(SEM) with EDS and the XRD was used for phase analysis.

## 2. EXPERIMENT AND METHODS

### 2.1 Materials and methods

The foil-fiber-foil method was adopted to fabricate the layered composite. Commercial pure titanium foils (100μm thick, ＞99.5% in purity), pure aluminum foils (100μm in thickness, ＞99.5% in purity) were cut into strips with a dimension of 40 mm × 60 mm for further use after cleaned carefully. C fibers (T700-3K with no nickel-plated, and T700-3K with nickel-plated) are alternately stacked. Monofilament diameter of C fiber is about 7μm, and the Ni coating layer with 300 nm thickness was deposited on the surface of C fiber by Electro deposition (CVD).

The layered composite specimens were prepared by the method of vacuum hot press sintering. The preparation process is shown in Table 1. Specimen was heated from room temperature to hot pressing temperature firstly, after the temperature reached to the setting-number, and a pressure of 5 MPa was applied to eliminate the space in adjacent foil and maintain time for 15 min, then pressurized to the maximum pressure and keep for some time, namely the holding time, then quickly cold to 600℃, and unloading, finally cool with the furnace. Moreover the purpose of delayed loading pressure was to keep the internal temperature of the specimen uniform and make sure that Al foils had well fluidity to fill the gap between fibers.

Table 1. Vacuum hot pressing process parameters

| Sample number | Hot pressing temperature(℃) | Maximum pressure (Mpa) | holding time （h） |
|---|---|---|---|
| 1 | 660 | 45 | 2.75 |
| 2 | 680 | 40 | 1.5 |
| 3 | 700 | 30 | 1 |
| 4 | 750 | 30 | 1 |

### 2. 2 Materials characterization

The specimens were ground and then polished by diamond suspensions. Microstructure and fracture surfaces were observed by scanning electron microscopy (SEM) combined with energy dispersive X-ray spectrometry (EDXS).Phase identification was performed by X-ray diffraction (XRD).

## 3. RESULTS AND DISCUSSION

### 3.1 Microstructure

Fig.1.shows the overall microstructure of Ti-Al-$C_f$ composites. As a whole, the layered microstructure of the material has a clear profile, and there is no obvious gap and cracks between the layers. As shown in the label, the white layer, the gray layer and the black part are the Ti, Al, and C fiber, respectively. Owing to the vacuum hot pressing temperature is lower than the melting point of Ti, the Ti layer exists in the form of solid phase during the hot pressing process. While Al is in the molten state, which was able to penetrate into the carbon fiber under the pressure. At the same time, the shape of the Ti layer can adjusted according to the Al-$C_f$ layer, so that the Ti layer was deformed obviously. In the Fig.1, the distribution of C fibers in the material is uneven, and the adjacent C fibers appear "bridging" phenomenon. Because the fiber spacing is small, the carbon atoms can diffuse among the two fibers, which will accelerate the reaction, resulting in a sharp decline in material properties.

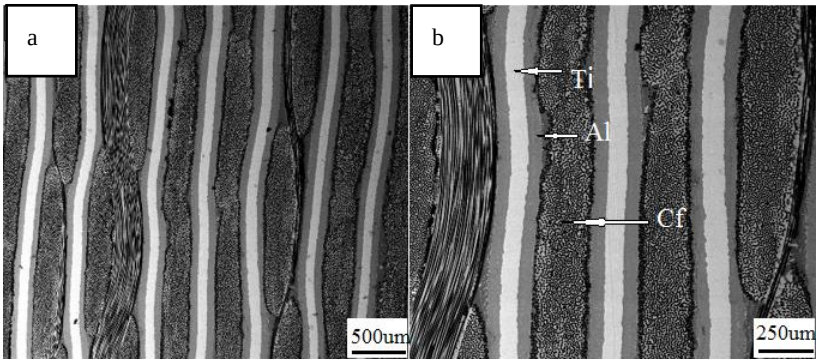
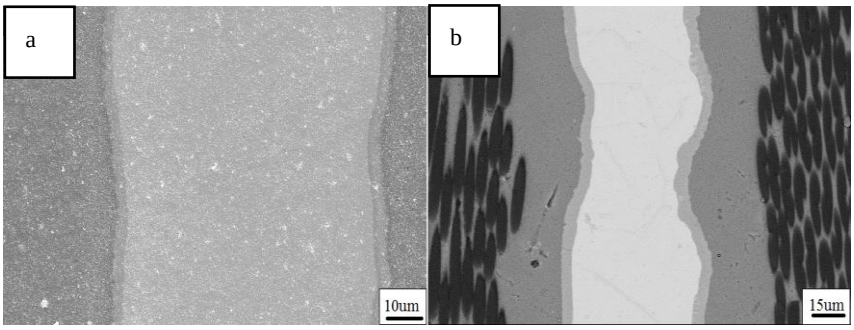



Fig.1. The overall microstructure of Ti-Al-$C_f$ composite: a) 100 times; b) 200 times

Fig.2 shows the microstructure of the interface of Ti-Al under the four experimental schemes. It can be seen from Fig.2 that the interface transition layer of Ti-Al in Fig. 2b) is obviously curved, except Fig.2b) the remainder of the figures, the interface of Ti-Al is basically smooth.



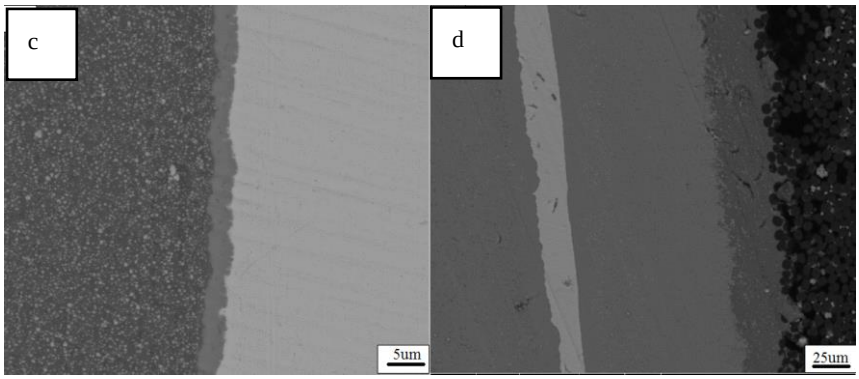



Fig.2. Microstructure Morphology of the interface of Ti-Al
a) 1#sample; b) 2 # sample; c) 3 # sample; d) 4 # sample

The thickness of the interfacial reaction layer of Ti-Al in each figure was measured, and the results are shown in Table 2.

Table 2: Ti-Al reaction layer thickness of each sample

| Sample number | Ti-Al reaction layer thickness ( μ m) |
|---|---|
| 1 | 4.2 |
| 2 | 6.0 |
| 3 | 3.5 |
| 4 | 104.5 |

Viewed from Fig.2 and Table 2, the thickness of interface layer of Ti and Al is different under different processes. As the temperature increased from 660℃ to 680℃, although the temperature rose, and the interface layer is still increased from 4.2μm to 6.0μm, which indicates that the temperature is the main factor affecting the thickness of the interfacial layer. The experimental results show that the thickness of the interfacial reaction layer decreased sharply at a temperature of 700 ℃, even less than that of the interface reacted at 660℃, and we suspect the interface layer should be continue to increase as the temperature increases. Due to the viscosity of the jump and the pressure began to play leading role on layer thickness. As shown in Fig.3,the pure Al temperature-viscosity curve[15], the pure Al kinematic viscosity increased with increasing temperature but appeared jumping at 700℃, and the mobility is decreased. Under this circumstance, the interfacial reaction weakened for the reduce of pressure and the holding time, and the thickness of interfacial layer decreased significantly. When the temperature increased to 750℃, the alloy viscosity decreased sharply, and the mobility increased sharply. At this case, the smaller the pressure and compress time is enough to exacerbate the interfacial reaction, and the thickness of interfacial layer increases.

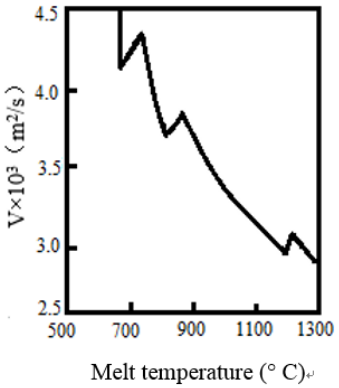



Fig.3. The relationship of pure aluminum liquid kinematic viscosity and temperature [15]

The morphology of C fiber and metal Al junction in 3# sample is illustrated in Fig.4. It is shown that the C fiber still presents the original vertical braided morphology, and the distribution of C fiber is uniform. From Fig.4b), it can be seen C fiber surface is relatively smooth, almost round, and part of the C fibers contact with each other. In this part, the Al liquid infiltrated into the C fiber fully, and the composite material is dense with no obvious folder aluminum layer, shrinkage and other defects, but only some individual small infiltration zones. In one word, the material has no obvious gap, and the structure of C fiber was not damaged.

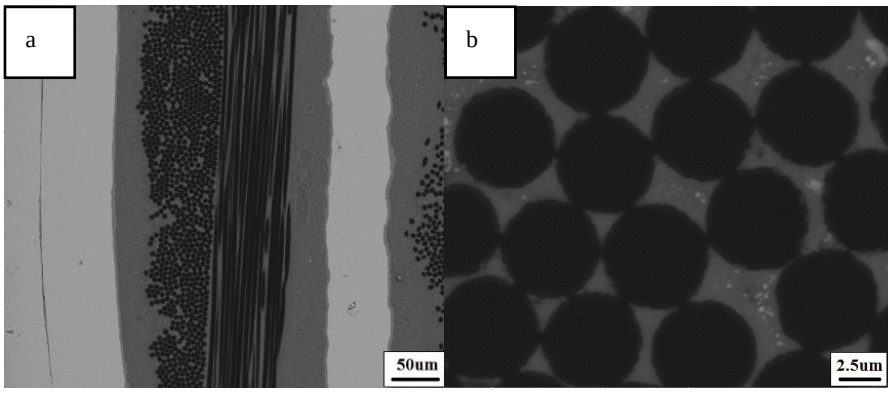



Fig.4 Microstructure Morphology of C-fiber and Al bonding
a) the overall effect of the map; b) local effect map

### 3.2 Phase analysis

As shown in Fig.5, the results of XRD analysis show that it is $TiAl_3$ phase at the interface of Ti/Al. The interfacial reaction product of the interface between C fiber and Al is $Al_4C_3$, which is generally rod-shaped, the aspect ratio is between 3 to 30, while it's found that only the presence of $Al_3Ni$ phase, not find $Al_4C_3$ phase for the nickel-plated C fiber was adopted, so the presence of nickel coating prevents the brittle phase $Al_4C_3$ generation, and protects the C fiber.

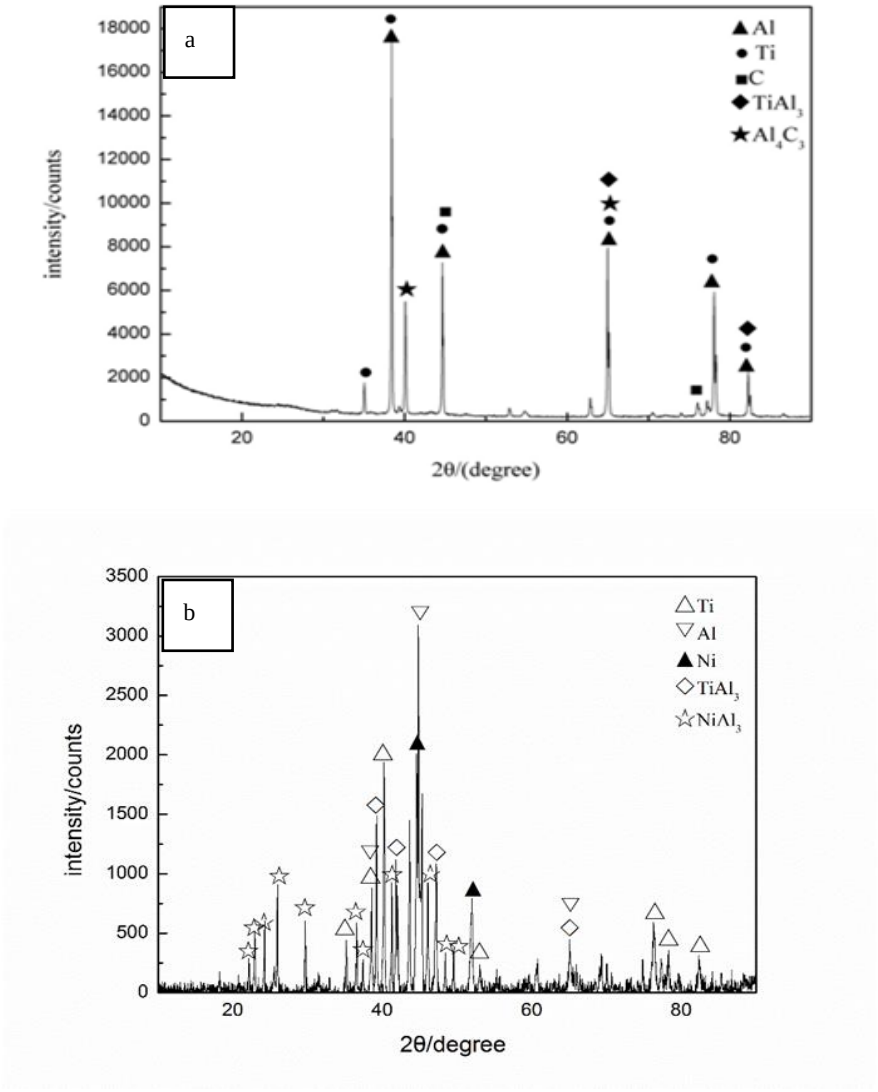



Fig.5 X-ray diffraction analysis

a) Nickel-free Ti-Al-$C_f$ composites ;b) Nickel-plated Ti-Al-$C_f$ composites

### 3.3 Line scanning and energy spectrum analysis

3.3.1 Scanning and Energy Spectrum Analysis of Ti/Al interface

Fig.6 a) shows the EDS energy spectrum the result of which is shown in Table3, and line scanning analysis results of the main elements of the Ti/Al interface is shown in Fig.6b). At the interface of Ti and Al, it can be seen that there is a certain concentration gradient and the composition gradient of Ti and Al can be seen as continuous. It can be concluded that Ti and Al atoms diffuse in a certain concentration, so Al is no longer the only diffusion component [16-18]. At the interfacial reaction layer of Ti/Al, the atomic percentage of aluminum atom and titanium atom is approximately 3:1, and it can be deduced that the reaction layer is mainly $Al_3Ti$ phase. It is because the free energy of $Al_3Ti$ is lower than that of $AlTi_3$ and AlTi at 273~1473K, and the Titanium-rich compounds $AlTi_3$ and AlTi are not formed when there is sufficient liquid Al in the reaction sintering process. The formation of $Al_2Ti$ and $Al_5Ti_2$ is subject to the formation of TiAl by a series of solid-liquid and solid-state reactions. The formation of $Al_2Ti$ and $Al_5Ti_2$ can be excluded from thermodynamics [19]. According to the diffusion reaction of Ti/Al

diffusion couple, it is concluded that the preferential growth of $TiAl_3$ is caused by the interfacial thermodynamics [20]. Thus, at the interface of Ti/Al, in the composite prepared by the reaction of the foil, the $TiAl_3$ is the only phase, as the reaction continue, the Al3Ti layer is completely formed until the aluminum foil is depleted. Especially the presence of liquid aluminum is more conducive to the formation of $Al_3Ti$ phase.

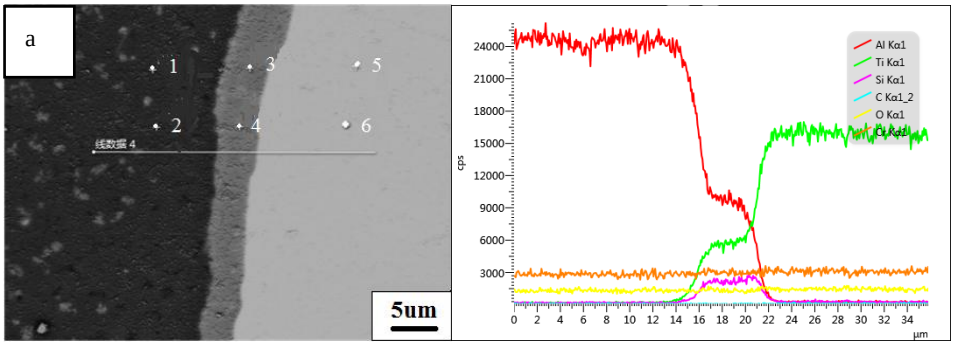



Fig.6. Spectrum and line scanning analysis of the interface region of Ti/Al

Table 3: EDS energy spectrum atomic fraction of main elements of Ti/Al interface

| Spectral label | location 1 | location 2 | location 3 | location 4 | location 5 | location 6 |
|---|---|---|---|---|---|---|
| Al（at%） | 100.00 | 100.00 | 75.46 | 74.21 | | |
| Ti（at%） | | | 24.54 | 25.79 | 100 | 100 |
| Total（at%） | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

3.3.2 Scanning and Energy Spectrum Analysis of the interface of $C_f$/Al

Fig.7. shows the EDS energy spectrum and line scan analysis of the main elements of the $C_f$/Al interface. Table 4 is the points marked, which corresponds in Fig.7 EDS spectrum. The value of atomic percentage of Al atoms and C atoms is roughly 4:3, which can be inferred that the reaction layer is $Al_4C_3$ phase. The presence of O elements is found in the EDS energy spectrum, owing to the limited vacuum of the vacuum hot press apparatus, so there is inevitably a small amount of O elements present in the material during the hot press process. From Fig.8 it can be seen the surface of C fiber is not smooth, in which there is a rod-like structure in the Al matrix. At the interface of $C_f$/Al, there is a concentration gradient of Al and C elements, and a certain degree of element concentration gradient occurs between Al atom and C atom. The thickness of the transition zone diffusion layer is about 2um, in which the main interfacial reaction between $C_f$/Al is Al (l) + C (S) = Al4$C_3$ (S) [21].The formation of Al4$C_3$ phase , which is needle (rod) -like, follows the nucleation and growth mechanism[22]. After the nucleation, the C atoms continue to diffuse to the front of $Al_4C_3$ compounds. However, the diffusion of the C atoms becomes difficult after the $Al_4C_3$ grows to a certain size, and the concentration of C atoms at front of reaction begin to decrease, so the reaction tends to slow [23].And the alternating atomic stack structure of $Al_4C_3$ in the prepared sample can effectively hinder the diffusion of C and Al atoms, as a result, the subsequent reaction will be weakened and the formation of $Al_4C_3$ phase is relatively reduced.

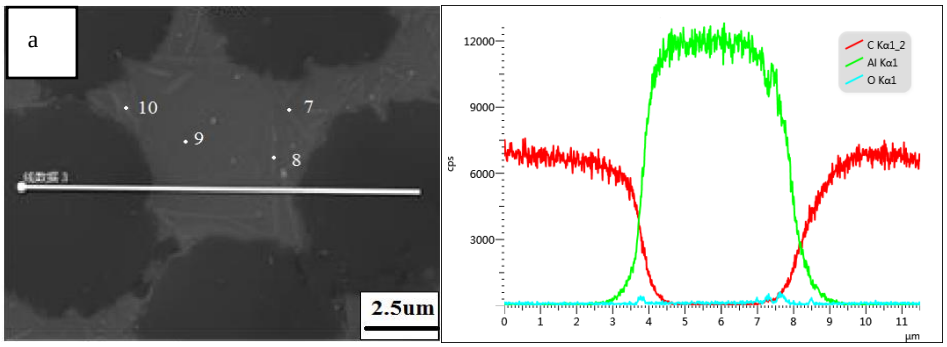



Fig.7. Energy spectrum and line scan analysis of the interface of $C_{f/}$ Al

Table 4: EDS energy spectrum atomic fraction of main elements of the interface of $C_f$/Al

| Spectral label | location 7 | location 8 | location 9 | location 10 |
|---|---|---|---|---|
| Al（at%） | 58.17 | 59.94 | 95.60 | 55.78 |
| C（at%） | 41.64 | 39.25 | 3.98 | 43.48 |
| O（at%） | 0.19 | 0.81 | 0.42 | 0.74 |
| Total（at%） | 100.00 | 100.00 | 100.00 | 100.00 |

At the C/Al interface reaction layer, the atomic percentage of Al atoms and Ni atoms is approximately 3:1, so it can be deduced that the reaction layer is $Al_3Ni$ phase. From the spectrum, which corresponds with Fig.8. and Table 5, it can be seen that the $Al_4C3$ phase is not formed at the C/Al interface. Because the formation of Al-Ni intermetallic compound [24]at the interface, the contact between the C fiber and Al was suppressed, and interfacial reaction was inhibited, which indicated that the nickel-plated layer can protect fiber, and prevent the formation of brittle phase $Al_4C_3$ by resulting in $Al_3Ni$ phase [25,26].The inhibition of $Al_4C_3$ phase, can weaken the interface to help improve the strength and elongation of composite materials [27].According to the EDS analysis, it was found that there was a small amount of C, the presence of C may be the diffusion between carbon fibers and the Al matrix during the preparation process, which results in loss of C in the fibers and changes the surface structure of C fibers.

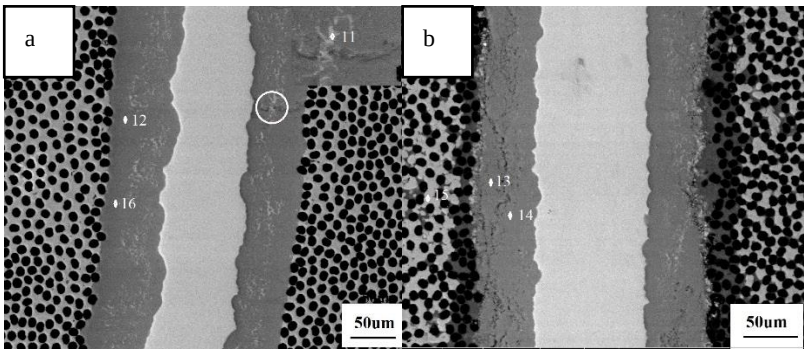



Fig.8. EDS spectra of the main elements in the interface of nickel-plated C-fiber reinforced composites

Table 5: EDS energy spectrum atomic fraction of main elements of $C_f$/Al interface

| Spectral label | location 10 | location 11 | location 12 | location 13 | location14 | location15 |
|---|---|---|---|---|---|---|
| Al（at%） | 62.88 | 58.01 | 72.46 | 70.11 | 76.3 | 59.95 |
| Ti（at%） | 6.53 | 19.63 | 27.13 | 26.28 | 0.2 | 21.77 |
| C（at%） | 16.45 | 22.03 | 0 | 3.21 | 0 | 17.89 |
| Ni（at%） | 14.13 | 0.33 | 0.41 | 0.4 | 23.5 | 0.4 |
| Total（at%） | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

## 4. CONCLUSION

Ti/Al/Al-$C_f$ multilayer layered composites were successfully prepared by by FFF method using carbon fiber fabric, Al sheets and Ti sheets. And it possesses a great potential as alternative fabrication route for Ti/Al/Al-$C_f$ with a good control over the fiber distribution. In the Hot pressing process, temperature plays a leading role on the interface reaction, and the secondary role is the pressure, the higher the temperature, corresponds the stronger the interfacial reaction. At the interface of Ti and Al, the main phase is $Al_3Ti$, Ti and Al atoms are diffused simultaneously. At the interface of Al and C fibers, there is Al, C element concentration gradient, the main phase is $Al_4C_3$.While the main generate phase of the nickel-plated C fibers was $Al_3Ni$,because the Ni layer effectively improves the chemical compatibility of the Al and C fiber, and inhibits the interfacial reaction.

## 5. ACKNOWLEDGEMENT

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## REFERENCES

[1] Wu Renjie. Development Status and Application Prospect of Metal Matrix Composites [J]. Aviation Manufacturing Technology, 2001, (3): 19 -21

[2] Li Jianhui, Li Chunfeng, Lei Tingquan. Progress in forming processing of metal matrix composites [J]. Materials Science and Technology, 2002,10 (2): 207-212

[3] Pawar P B, Utpat A A. Development of Aluminum Based Silicon Carbide Particulate Metal Matrix Composite for Spur Gear [J]. Proceda Materials Science, 2014, 6: 1150-1156.

[4] Li Dan, Wu Jianjun, Dong Yun. Preparation of Continuous Fiber Reinforced Composites [J]. Materials Review: Online Edition, 20 08 (5): 22-24.

[5] Pang Jincheng. Study on Synthesis Mechanism of TiAl Matrix Composites Based on SiCp /Al-Ti System [J]; Harbin Institute of Technology;

[6] QU Hai-tao, REN Xue-ping, HE Hong-liang, et al. In-situ synthesis and control of silicon carbide fiber reinforced titanium matrix and its dynamic analysis [J]. Rare Metal Materials and Engineering, 2014, 2: 20-22.

[7] Ma Li, Sun Yue, He Xiao dong． Preparation and Performance of large-sized Ti/Ti-Al micro-laminated composite [J]. Rare Metal Mater Eng, 2008, 37(2):325.

[8] Youssif Y G. Non-linear design and control optimization of laminated composites doubly curved shell [J]. Compos Struct, 2009, 88(3):468.
[9] Shiau Le-Chung, Kuo Shih-Yao, Chen Cheng-Yuan. Thermal buckling behavior of composites laminated plates [J].compos Struct, 2010, 92(2):508.
[10] Guo Xin, Ma Qin, Ji Genshun, et al. (6): 66 (in Chinese with English abstract) [J]. Journal of Materials Research, 2007,21 (6): 66.
[11] Zhou Xiya, Dong Wei. Progress in Research on Laminated Ceramic Composites [J]. Chinese Journal of Ceramics, 2007,43 (7): 11.
[12] LIU Lian-tao, SUN Yong.Study on Progress of Fiber Reinforced Aluminum Matrix Composites [J]. South China Metal, 2008, (6): 1-4.
[13] Brian R，Yuen H C，Lee W B. The processing of metal matrix composites-an overview[J]. Journal of Materials Processing Technology，1997,63：339-353.
[14] Mao, X.N., Zhang, P. S.,YU,L.L.. The research progress of fiber reinforced titanium matrix composites . Rare Metal Express. 2005, (24)5:1~6.
[15] Geng Haoran, Liu Guodong, Sun Minhua, et al. Research and prospect of the correlation between metal melt viscosity and its microstructure [C]. China Materials Seminar.
[16] Van Loo F J J, Rieck G D. Diffusion in the titanium-aluminium system—II. Interdiffusion in the composition range between 25 and 100 at.% Ti[J]. Acta Metallurgica, 1973, 21(1): 73-84.
[17] Luo J G, Acoff V L. Interfacial reactions of titanium and aluminum during diffusion welding[J]. WELDING JOURNAL-NEW YORK-, 2000, 79(9): 239-s.
[18] Xu L, Cui Y Y, Hao Y L, et al. Growth of intermetallic layer in multi-laminated Ti/Al diffusion couples[J]. Materials Science and Engineering: A, 2006, 435: 638-647.
[19] Kattner U R, Lin J C, Chang Y A. Thermodynamic assessment and calculation of the Ti-Al system[J]. Metallurgical and Materials Transactions A, 1992, 23(8): 2081-2090.
[20] Liu J P, Luo L S, Yan-Qing S U, et al. Numerical simulation of intermediate phase growth in Ti/Al alternate foils[J]. Transactions of Nonferrous Metals Society of China, 2011, 21(3):598-603.
[21] ZHAO Chang-zheng, LIU Xin-xiang.Study on Interface Microstructure of Carbon Fiber Reinforced Aluminum Matrix Composites [J]. Journal of Shanghai Jiaotong University, 1992,26 (6): 125-128.
[22] Diwanji A P，Hall I W. Fibre and fibre-surface treatment effects in carbon/aluminium metal matrix composites[J]. Journal of Materials Science，1992，27：2093-2100.
[23] Khan I H. The Effect of Thermal Exposure on the Mechanical Properties of Aluminum-Graphite Composites[J]. Metallurgical Transactions A，1976，7A：1281-1289.
[24] Ralph B，Yuen H C，Lee W B. The processing of metal matrix compositesan overview[J]. Journal of Materials Processing Technology，1997，63：339-353.
[25] D. Chun-feng, Z. Xue-xi, W. Dezun. Chemical stability of carbon nanotubes in the 2024Al matrix. Materials Letters. 2007, (61):904~907.
[26] M. H. Vidal-Setif, M. Lancin, C. Marhic, R. et al. On the role of brittle interfacial phases on the mechanical properties of carbon fiber reinforced Al-based matrix composites Materials Science and Engineering A. 1999, (272):321~333.
[27] Li S H，Chao C G. Effects of Carbon Fiber/Al Interface on Mechanical Properties of Carbon-Fiber-Reinforced Aluminum-Matrix Composites[J].Metallurgical and Materials Transactions A，2004，35A：2153-2160.