Effects of Joining Conditions on Microstructure and Mechanical Properties of C_f/Al Composites and TiAl Alloy Combustion Synthesis Joints

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Received: 19 April 2014 / Revised: 13 October 2014 / Published online: 17 February 2015
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Abstract C_f/Al composites and TiAl alloy were joined by combustion synthesis in different joining conditions. Effects of additive Cu, joining temperature and holding time on joint microstructure and shear strength were characterized by employing DTA, SEM, EDS, XRD and shear test. Results show that the additive Cu in the Ti–Al–C interlayer could significantly decrease the reaction temperature owing to the emergence of Al–Cu eutectic liquid. Reaction degree of the interlayer was influenced by joining temperature and holding time. Due to the barrier action of formed TiAl₃ layer, reaction rate of Ti and Al was determined by the atoms diffusion. The reaction between Ti and Al was more sensitive to the joining temperature rather the holding time. The joints shear strength was influenced by joining condition directly. The maximum shear strength of CS joints was 25.89 MPa at 600 °C for 30 min under 5 MPa. Interface evolution mechanism of the CS joint was analyzed based on the experimental results and phase diagram.

KEY WORDS: C/Al composite; TiAl alloy; Combustion synthesis; Interface microstructure; Formation mechanism

1 Introduction

Carbon fiber reinforced aluminum matrix composites (C_f/Al composites) have been regarded as the new promising structure materials in aerospace field [1, 2] due to their lightweight, high specific strength and stiffness, excellent electrical and thermal conductivity. TiAl alloy has also received special attention for the application in elevated temperature owing to its high melting point and oxidation resistance [3]. Compared with the nickel-based superalloys, TiAl alloy has closed working temperature but low density, which makes it to be an ideal replacement of the nickel-based superalloys [4]. The joining of C_f/Al composites and

TiAl alloy can take full use of their advantages and further expand their application.

However, the significant differences between the C_f/Al composites and TiAl in the properties make it difficult to obtain the sound joint. Due to its high melting point, brazing temperature of the TiAl alloy was usually over 800 °C [5, 6], which is much higher than the melting point of C_f/Al composites. When the Al-based fill metal was applied, the application temperature of the joint would be limited [7]. In diffusion bonding, high pressure applied on the composites would damage the connection between reinforced fibers and matrix [8]. In addition, when fusion welding was conducted, the reinforced C_f would react with melted aluminum and generate much brittle Al₄C₃ in the joint [9]. Thus, reliable joint could not be achieved by conventional welding methods, and novel welding method must be developed.

Combustion synthesis (CS) is a promising technique and can be used in joining field [10, 11]. Materials were joined by the localized heat released by the exothermic reaction of

Available online at <http://link.springer.com/journal/40195>

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interlayer without thermal damage. Reaction products were usually intermetallics with high melting points, which could make the joint has high application temperature. Successes have also been achieved in the joining of TiAl alloy and ceramics. The properties of CS joints depend on the joining process. Under different joining conditions, different reaction products will form and lead to the change in the microstructure and the joint mechanical properties. Cao *et al.* [12] have discussed the effect of the reaction heat on the microstructure and the shear strength of TiAl/TiAl–Al–C/TiAl reactive joints. It has been found that the reaction heat had a considerable effect on the thickness of TiAl₃ reaction layer and the density of products. The highest shear strength was achieved when the adiabatic temperature of the interlayer was 2491.5 K with a composition of Ti50–Al35–C15 (at.%). Meanwhile, Cao *et al.* [13] have studied the influence of joining pressure and applied Ag-based brazing alloy on the microstructure and mechanical properties of TiAl/TiAl SHS joints. They found that product density was influenced by the joining pressure. The density increased greatly, and no voids were found in the interlayer when the Ag-based brazing alloy was applied.

In present study, the effects of additive Cu, joining temperature and holding time on the joint microstructure and the shear strength were evaluated. Furthermore, formation mechanism of the C_f/Al composites and TiAl alloy CS joint has been analyzed.

2 Experimental

The C_f/Al composites applied in this study had a fiber volume fraction of 50% and metal matrix of 6,061 aluminum alloy. The C_f/Al composites were achieved through

extrusion casting method, with a density of 2.189 g cm^{−3}. The microstructure of the C_f/Al composites is shown in Fig. 1. TiAl alloy had the nominal composition of Ti–48Al–7V–0.3Y (at.%). The C_f/Al and TiAl were cut into 5 mm × 5 mm × 3 mm and 12 mm × 8 mm × 2 mm, respectively, for the microstructure analysis and the shear test. All joined surfaces were polished by SiC papers up to grit 1,000 and ultrasonically cleaned by acetone for 5 min prior to the joining.

Commercial powders of high purity Ti (99.5%, 325 mesh), Al (99.5%, 325 mesh), C (99.5%, 1,250 mesh) and Cu (99.5%, 325 mesh) were used in this study. Appropriate amounts of Ti, Al, C and Cu powders were weighed out according to 32Ti–16Al–C (wt%) and 32Ti–16Al–C–Cu (wt%). Then, the powder mixtures were milled at room temperature in a hardened steel bowl using Al₂O₃ balls for 2 h, with the rotation speed of 300 r/min. And the weight ratio of Al₂O₃ ball to powder was 10:1. The milled powders were uniaxially cold-pressed into cylindrical shape of 10 mm diameter and 1 mm height under the pressure ranging from 10 to 20 MPa. For direct CS joining, the green compact was applied between C_f/Al and TiAl, which is shown in Fig. 2. Then, the sandwiched structure was joined in the radiation heating vacuum diffusion welding machine, in which the studio vacuum degree was able to reach 1.33×10^{-4} Pa. The heating rate was set at 15 °C/min. After the joining, all the specimens were furnace-cooled to room temperature.

To characterize the microstructure, the joints were transected and processed to be standard metallographic samples prior to the observation. Afterward, the samples were examined by means of Hitachi S-4700 scanning electron microscope (SEM) equipped with energy-dispersive spectrometer (EDS). Then, the joints were analyzed by X-ray diffraction (XRD) with CuK_α radiation. As shown in Fig. 3, room temperature shear test was conducted

Fig. 1 Microstructure of the C_f/Al composites

Fig. 2 Schematic diagram of the joining system

Fig. 3 The schematic of the joint shear test

employing an Instron-1186 universal testing machine by means of a specially designed fixture at a crosshead rate of 0.5 mm/min.

3 Results and Discussion

3.1 Effect of Additive Cu on the Ignition Temperature of Ti–Al–C Interlayer

The appearance of liquid is the key to the ignition of Ti–Al–C interlayer, according to previous study [10]. For this reason, Cu was added in the Ti–Al–C interlayer. The Al–Cu eutectic liquid, formed at 548.2 °C [14], can decrease the reaction temperature and join the C_f/Al composites and TiAl alloy at lower temperature. Differential thermal analysis (DTA) test of the interlayer was conducted before the joining. Figure 4 represents the DTA curves of Ti–Al–C and Ti–Al–C–Cu interlayer, obtained with the heating rate of 10 °C min^{−1} under argon flow.

It is noted that an endothermic peak and exothermic peak were detected both in the Ti–Al–C and Ti–Al–C–Cu interlayer. In the Ti–Al–C curve, the endothermic peak started to appear at 660 °C, which is the melting point of Al and then came the following exothermic peak. With the addition of Cu, the curve changed obviously. Owing to the formation of Al–Cu eutectic liquid, the location of the endothermic peak moved forwards 110 °C and reached 550 °C. According to the viewpoint of Naplocha *et al.* [15], the formation of eutectic liquid strongly increases the dissolution and diffusivity of Ti and accelerates the reaction rate. Sharp reaction usually follows in the CS reaction. Meanwhile, not only the location of the endothermic peak but also the exothermic peak moved forward with the addition of Cu, as illustrated in Fig. 4, which could allow lower joining temperature in this study.

Fig. 4 DTA curves of the interlayer

3.2 Interfacial Microstructure of the CS Joint

The backscattered electron images of the C_f/Al/Ti–Al–C–Cu/TiAl joint at 600 °C for 30 min under 5 MPa were shown in Fig. 5. As shown in Fig. 5a, reliable bonding between the interlayer and substrates formed, and the joint was free from structural defects such as voids and cracks. In order to further investigate the interfacial microstructure, more details are presented in a larger visual field, as shown in Fig. 5b–d. The EDS results taken from different phases are included, as shown in Table 1.

The microstructure on TiAl side is shown in Fig. 5b. Adjacent to the TiAl substrate, one obvious continuous gray reaction layer was observed, which demonstrated the reaction between the TiAl substrate and interlayer. According to the DTA curves in Fig. 4, the Al–Cu eutectic liquid formed at about 550 °C and high exothermic reaction would be initiated later. During the joining, the Al–Cu eutectic liquid contacted with the TiAl substrate. Al atoms in the eutectic liquid reacted with the TiAl substrate and produced the TiAl₃ layer according to the following reaction:

According to the research of Shiue *et al.* [16], TiAl₃ layer would also form due to the reaction between TiAl and Al-based braze alloys. Simultaneously, the gray reaction layer (marked by A) had the average composition of 23.52 Ti, 76.48 Al (at.%), which could be confirmed as TiAl₃ phase and prove the correctness of above guess.

Figure 5c shows the microstructure of the C_f/Al side. Some white needle-like phases formed and distributed in the aluminum matrix. According to above analysis, the Al–Cu eutectic liquid emerged first in the joining. The freedom of Al and Cu atoms was improved and gave atoms the abilities of diffusing to the aluminum matrix. The interlayer bonded well with the composites under the sufficient

Fig. 5 Microstructure of the joint: **a** the whole joint; **b** the TiAl side; **c** the C_f/Al side; **d** the interlayer

Table 1 EDS compositional analysis results of the different marked regions in Fig. 5d

Region	Al	Cu	Ti	C	Possible phase
A	76.48	–	23.52	–	TiAl ₃
B	66.44	33.56	–	–	Al ₂ Cu
C	–	–	100	–	Ti
D	100	–	–	–	Al
E	76.40	–	23.60	–	TiAl ₃
F	38.42	–	–	61.58	Al ₄ C ₃
G	65.69	34.31	–	–	Al ₂ Cu

diffusion of Al atoms. Simultaneously, Cu atoms entered the aluminum matrix and reacted with Al atoms, produced the needle-like Al₂Cu phase (marked by B) according to the reaction as:

The Al₂Cu phase was also detected in the research by Niu *et al.* [17]. Meanwhile, some gray phase, which was

confirmed to be TiAl₃, formed between the Ti particles and the aluminum matrix. A few of C_f transformed to be the black particles on the C_f/Al side.

The microstructure of Ti–Al–C–Cu interlayer is shown in Fig. 5d. Some reactions occurred in the interlayer, and several different phases formed. However, the reaction between Ti and Al was not complete. Large blocked residual Ti (marked by C) distributed in the gray Al (marked by D). Under the heating effect in the joining, the Ti particles reacted with the Al–Cu eutectic liquid and produced the thin dark gray TiAl₃ layer (marked by E in Fig. 5d) according to the following reaction:

The carbon particles reacted with Al and formed the black Al₄C₃ (marked by F) near the TiAl₃ layer. Moreover, the Al–Cu liquid solidified in the cooling process, and the Al atoms reacted with the Cu atoms and produced the needle-like Al₂Cu phase (marked by G).

According to above analysis, a TiAl₃ layer with a thickness of about 15 μm formed adjacent to the TiAl

Fig. 6 XRD result of the interlayer

substrate. In the interlayer, Ti reacted with Al and thin TiAl_3 layer formed around Ti particles. For the large content of Ti and Al, their reaction was the main reaction in the interlayer. However, the reaction was not complete, and large quantity of residual Ti and Al remained in the interlayer. The formed TiAl_3 layer conducted as a barrier and cut off the contact between the Ti and C. Thus, Ti and C reaction did not occurred. The carbon particles reacted with Al and some Al_4C_3 formed in the interlayer and C_f/Al side. During the joining process, the Cu elements diffused and generated the white needle-like Al_2Cu in the C_f/Al and interlayer, which could work as the reinforced phase and enhance joint shear strength. Meanwhile, XRD analysis of the interlayer was conducted, as illustrated in Fig. 6. TiAl_3 , Al_2Cu , Al and Ti were detected and proved the above guess. However, the Al_4C_3 could not be detected in the XRD diffraction pattern owing to its low content.

3.3 Effects of Joining Temperature and Holding Time on the Joint Microstructures

The backscattered electron images of CS joints obtained at different joining temperatures are shown in Fig. 7. As shown in the images, the joining temperature had a great influence on the interfacial microstructure.

As the increase of joining temperature, the reaction between Ti and Al became complete gradually, and the content of residual Ti and Al decreased. Due to sufficient reaction in the interlayer, large scale of TiAl_3 phase formed. Some tiny voids dispersed in the original interlayer before the joining, and they were still not easy to identify in Fig. 7a. However, the voids gathered gradually and became larger as the reaction proceeded under the effect of atom transfer and shrinkage by solidification from high temperature. Adjacent to the C_f/Al , bonding between the C_f/Al and interlayer got stronger at higher temperature. As the

research by Zhang *et al.* [18], the content of Al_2Cu phase in the C_f/Al also increased. Moreover, the TiAl_3 layer on TiAl side thickened distinctly with increasing the joining temperature.

Figure 8 shows the joint microstructures at different holding time. As the extension of holding time, reaction degree of the interlayer increased slightly rather than significantly. The content of residual Ti and Al slightly decreased, but a large quantity of light blocked Ti was still visible even for 60 min. On the TiAl side, the thickness of TiAl_3 layer increased gradually as the extension of holding time but was still not so significantly compare with Fig. 7. Combining Figs. 7 and 8 together, it could be seen that the reaction between Ti and Al was more sensitive to the joining temperature rather holding time. The joining temperature played a decisive role in the formation of TiAl_3 product and TiAl_3 layer. When the joining temperature was constant, the change in holding time had a small effect on the joint interface microstructure.

3.4 Microstructure Evolution of CS Joint

Based on the experimental results and related phase diagrams, a conceptual joint microstructure evolution model is illustrated in Fig. 9. The whole CS joining process can be divided into the following stages:

3.4.1 The Physical Contact

According to the DTA curves of Ti–Al–C–Cu interlayer in Fig. 4, the Al–Cu eutectic liquid didn't emerge until the temperature reached 550 °C. When the temperature was lower than 550 °C, the lack of liquid led to lower atomic activity. No significant reaction occurred in the joining system. The interlayer and base metal only had physical contact under joining pressure. The contact area was limited, and solid-phase reaction in the interlayer was very weak. With further increase of the temperature, the interlayer became softer and the contact got close gradually, as shown in Fig. 9a.

3.4.2 Reaction in the Ti–Al–C–Cu Interlayer

When the temperature reached 550 °C, Al–Cu eutectic liquid appeared in the interlayer, filled the gap through capillarity and surrounded the Ti, C particles. Atomic activity of Al increased significantly owing to the emergence of eutectic liquid. Intense reaction between the Al–Cu eutectic liquid and Ti particles occurred, and one TiAl_3 layer formed around the Ti particles. Large quantity of heat released and caused the rapid increase of the temperature. When the TiAl_3 layer reached a certain thickness as the reaction progress, it worked as a diffusion barrier and cut

Fig. 7 Microstructures of the joints at different joining temperature ($t = 30$ min): **a** $T = 500$ °C; **b** $T = 550$ °C; **c** $T = 600$ °C; **d** $T = 650$ °C

off further reaction. C particles reacted with Al–Cu eutectic liquid and Al_4C_3 formed, as shown in Fig. 9b. With the increase of temperature and the extension of holding time, the atomic diffusion enhanced. Some Al and Ti atoms diffused across the TiAl_3 layer and reacted with each other. Content of TiAl_3 phase increased, and the amount of residual Ti decreased. The reaction of Ti and Al became complete gradually.

3.4.3 Reaction Between the Interlayer and Substrates

As the reaction progress, more Al–Cu eutectic liquid formed, and the contact between the interlayer and base metals became complete. Under the effect of exothermic reaction, the temperature of Ti–Al–C–Cu interlayer increased significantly and was close to the adiabatic temperature (higher than 1,527 °C). Local aluminum matrix of C_f/Al composites, which contacted with the interlayer,

melted. Cu atoms diffused to the aluminum matrix. Needle-like Al_2Cu formed and distributed in the aluminum matrix. Besides, molten Al in the interlayer reacted with TiAl. A TiAl_3 reaction layer formed on the TiAl side, as shown in Fig. 9c.

3.4.4 Formation of the Final Joint

The temperature of the joining system decreased after the exothermic reaction. Localized molten aluminum matrix and adjacent Al–Cu eutectic liquid solidified. A reliable bonding between the C_f/Al and interlayer formed. Al_2Cu phase separated out when the temperature was below the Al–Cu eutectic temperature. Liquid disappears in the joining system. The reaction rate declined gradually until stops. Eventually, the final joint with a typical structure of $\text{C}_f/\text{Al}/\text{Al}_2\text{Cu} + \text{C}_f/\text{Al}/\text{TiAl}_3 + \text{Al}_2\text{Cu} + \text{Al}_4\text{C}_3/\text{TiAl}_3/\text{TiAl}$ formed, as shown in Fig. 9d.

Fig. 8 Microstructures of the joints at different holding time ($T = 600\text{ }^{\circ}\text{C}$): **a** $t = 10\text{ min}$; **b** $t = 20\text{ min}$; **c** $t = 30\text{ min}$; **d** $t = 60\text{ min}$

3.5 Room Temperature Shear Strength of the Joint

The relationship between the joining parameters and joint shear strength is illustrated in Fig. 10. The specimens joined at $600\text{ }^{\circ}\text{C}$ for 30 min demonstrated the highest average shear strength of 25.89 MPa. In addition, the joint strength then decreased with the increase of joining temperature and holding time.

When the joining temperature was low, the reaction in the interlayer was so feeble that only little heat released. The atom diffusion was restrained, and bonding between the interlayer and substrates was very weak, which caused the low strength. With the increase in the joining temperature, the reaction degree and the thickness of TiAl_3 layer increased. Joint strength reached the peak in $600\text{ }^{\circ}\text{C}$. According to the research of Li *et al.* [19], the interface bonding of C_f and aluminum matrix is mainly based on their chemical reaction. When the temperature increases to $650\text{ }^{\circ}\text{C}$, the interface reaction of reinforced carbon fibers and aluminum in the composites became severe. Large

quantity of brittle Al_4C_3 formed, and the performance of C_f/Al was damaged seriously. Besides, some carbon fibers reacted with the interlayer. The brittle Al_4C_3 formed and distributed in the C_f/Al /interlayer interface. Under the effect of shrinkage by solidification from high temperature, microcrack occurred on the C_f/Al side. During the shear test, the failure process started when the microcrack connected and propagated to the whole joint. The fractograph of joint at $650\text{ }^{\circ}\text{C}$ for 30 min is shown in Fig. 11. The strength was only 11.37 MPa. On the TiAl side, the brittle TiAl_3 layer became too thick and caused the biggish interfacial stress. Therefore, the shear strength decreased significantly in $650\text{ }^{\circ}\text{C}$. The effect of the holding time on the joint strength was similar with the joining temperature. The joint strength increased firstly as the extension of holding time. But the formation of TiAl_3 was not so sensitive to the holding time, so the continuous extension of the holding time had a small effect on the joint strength. The joint strength reached maximum 25.89 MPa at $600\text{ }^{\circ}\text{C}$ for 30 min.

Fig. 9 Schematic drawing of formation mechanism of C/TiAl and TiAl CS joint with Ti–Al–C–Cu interlayer: **a** physical contact; **b** reaction in the Ti–Al–C–Cu interlayer; **c** reaction between the interlayer and substrates; **d** formation of the final joint

Fig. 10 Effects of the joining parameters on the joint shear strength: **a** joining temperature; **b** holding time

Fig. 11 Fractograph of the joint at 650 °C for 30 min

4 Conclusions

C_f/Al composites and TiAl alloy have been successfully joined by CS joining with Ti–Al–C–Cu interlayer. Additive Cu significantly lowers the reaction temperature of Ti–Al–C interlayer benefited from the Al–Cu eutectic liquid formed at 550 °C. One TiAl₃ layer and some needle-like Al₂Cu form on two sides, respectively. C_f at the interface and C particles react with Al–Cu eutectic liquid, and Al₄C₃ forms. Besides, Ti particles react with the eutectic liquid leading to the TiAl₃–Ti circular structure. Al₂Cu separates out of the eutectic liquid and distributes in the residual Al. The joining temperature and the holding time have direct effect on the joints microstructure. Owing to the barrier action of formed TiAl₃ layer, further reaction between Ti and Al in the interlayer is determined by atom diffusion. The reaction between Ti and Al is more sensitive to joining temperature rather holding time. The change in the holding time has a small effect on the joint microstructure compared with the joining temperature. The joint formation can

be divided into four parts, which are physical contact, reaction in the Ti–Al–C–Cu interlayer, reaction between the interlayer and substrates, and formation of the final joint. The maximum shear strength of joint is 25.89 MPa at 600 °C for 30 min under 5 MPa in this experiment. Higher temperature will damage the C_f/Al seriously and decrease the joint shear strength.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (No. 51075101).

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