Microstructure and Mechanical Properties of C/C Composite/TC17 Joints with Ag-Cu-Ti Brazing Alloy

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Abstract: Carbon/Carbon composite (C/C) was vacuum brazed to titanium alloy (TC17) using Ag-Cu-Ti brazing alloy. The effects of brazing temperature on the interfacial microstructure and joint properties were investigated by energy dispersive spectrometer (EDS), a scanning electron microscope (SEM), X-ray diffraction (XRD) and Gleeble1500D testing machine. Results show that C/C composite and TC17 were successfully brazed using AgCuTi brazing alloy. Various phases including TiC, Ag(s, s), Cu(s, s), Ti3Cu4, TiCu, and Ti2Cu were formed in the brazed joint. The maximum shear strength of the brazed joints with AgCuTi brazing alloy was 24±1 MPa when brazed at 860°C for 15 min.

1. Introduction
Carbon/carbon (C/C) composites have been applied in aviation and aerospace fields for their excellent physical properties, such as low density, very high thermo-elastic stability, high thermal conductivity, good thermal shock resistance, fatigue resistance, and excellent mechanical properties at high-temperature [1, 2]. C/C composite is both difficult and expensive to fabricate into large or complex shaped components due to its properties and the need of reliable integration of components into a structure requires an effective technique for their joining. Brazing between C/C composites and metal/alloy attracted more and more attention due to their wide potential engineering applications [3, 4]. There is a requirement to join them to metals/alloy in many engineering applications of C/C composite, such as TC17 titanium alloy. TC17 titanium alloy (nominal composition of Ti-5Al-4Mo-4Cr-2Sn-2Zr, for the convenience, Ti-5Al-4Mo-4Cr-2Sn-2Zr is marked as TC17 alloy in the following figures.) accounts a large proportion of the total usage of titanium alloy due to the excellent toughening and high temperature property [5]. In the past decades, many processes have been developed for joining C/C composite to Titanium alloy. Due to its simplicity, cost-effectiveness and perfect adaptability of joint size and shape, brazing has been widely applied [6-9]. Two main problems of the joining of C/C composites to metals are the wetting of C/C composites by the liquid brazing alloy and the large coefficient of thermal expansion (CTE) mismatches between C/C composite (CTE\textsubscript{C/C}=0-2 \times 10^{-6} \text{ K}^{-1}) and titanium alloy (CTE\textsubscript{Titanium alloy} =8.4-9.9 \times 10^{-6} \text{ K}^{-1}) which causes high residual stress, and consequently results in the degradation of joint during the cooling process [8, 9]. In order to over these problems, a soft interlayer at the interface or low-CTE reinforcements in the joining material has been applied. Song et al. [2] studied a novel Cu/TiCuZrNi composite braze used in C/C composites and Ti6Al4V brazed joint. The Cu composite interlayers could release the residual stresses and increase the mechanical properties at the joint interface. Wang et al. [10] reported a novel type of three-dimensional graphene-reinforced Cu foam used as an interlayer for brazing seam. The extremely low CTE of graphene and the good plastic deformation capacity of Cu foam are both conductive to
reducing the thermal residual stress during the cooling process and increasing the shear strength of the joint. Yang et al. [11] reported that the elastic deformation of Ni foam was beneficial for stress release for diffusion joining ZrB2SiC and Nb. Zhu et al. [12] used different thicknesses of Ni foam interlayer and verified that Ni foam could play the role as a buffer layer to reduce the residual stress. Moreover, many studies suggested the addition of low CTE materials (such as carbon fibers and carbon nanotubes, ceramic fibers, particles, etc.) into brazing alloy could mitigate residual stress and consequently improve the mechanical properties of a composite-metal joint [10]. Dai et al. [13] verified the B4C reinforced AgCuTi composite filler could reduce or eliminate residual stress in the interfacial region to improve the mechanical properties of the joints. Song et al. [14] used carbon nanotubes (CNTs) as reinforcements in the TiCuZrNi brazing alloy for joining C/C composites to Ti6Al4V. Zhao et al. [15] used a novel nano-Si3N4 particle as reinforcements in the AgCuTi composite filler for the brazed joint of Ti6Al4V and Si3N4 ceramic. Zhou et al. [16] verified AgCuTi composite filler strengthened by nano-Al2O3 improved the shear strength of brazed joint between C/C composite and TC4 alloy. The mismatch in CTE between substrates and brazing seam could be reduced due to the composite fillers by bring in fibers or tiny ceramic particles with lower CTE into traditional brazing fillers [16].

In this work, vacuum brazing of TC17 alloy and C/C composite with active Ag-Cu-Ti filler metal is performed at different temperature. The interface microstructures and evolution of the TC17/AgCuTi/C/C composite joint are analyzed and the mechanical properties of the joints are discussed.

2. Materials and Experimental Procedures

The base materials are C/C composite and TC17 alloy. C/C composites were obtained from Boyun New material Co., LTD, China, which was 2D entwined and 3D punctured. The C/C composite is a kind of carbon matrix composite reinforced by carbon fiber. The C/C composite was cut into blocks with a dimension of 5mm × 10mm × 5mm by spark cutting. Before brazing, the TC17 alloy was cut into blocks with a dimension of 5mm × 10mm × 5mm. A 50 μm thick Ag68.83-Cu26.77-Ti4.4 (wt.%) foil was used as filler metal (obtained from AECC Beijing Institute of Aeronautical Materials), which was melted in a vacuum high-frequency induction furnace using particles of titanium, copper and silver. The microstructures of C/C composite and TC17 alloy are shown in Figure 1. The joining surfaces of both materials and filler foils were ground by 1000 grits silicon carbide paper and then cleaned ultrasonically for 15 min in ethanol and then dried by air blowing. The Ag-Cu-Ti foil was sandwiched between the C/C composite and TC17 alloy samples and a slight pressure was applied to maintain good contact between the joining surfaces and then the brazing assemblies were carefully placed into the vacuum furnace. The brazing assembly schematic is shown in Figure 2 (a).

Figure 1. Microstructure of base materials: (a) TC17 alloy (b) C/C composite

The brazing was performed in a vacuum furnace under the vacuum of 1×10⁻³ Pa. The brazing temperature adopted in this study is 840°C-920°C while the temperature interval is 20°C. The brazing
assemblies were first heated to 750°C at a rate of 15°C/min and held for approximately 10min, then to the brazing temperature (840°C-920°C) at a rate of 10°C/min and held at brazing temperature for 15min. Subsequently, the brazing couples were held for 15 min at brazing temperature, then cooled down to 100°C at a rate of 10°C/min. Finally, the joints were cooled down to room temperature in the vacuum furnace.

The cross-sections of the brazed joints were perpendicular to the brazed surface and prepared for metallographic analysis. The microstructures of the joints were characterized by scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). Furthermore, the microstructure of TC17 side was investigated by X-ray diffraction (XRD) to identify the interfacial phases accurately. The shear test was performed at a constant speed of 0.5mm/min by the Gleeble 1500D at room temperature and the schematic diagram of shear test is shown in figure 2(b). At least five samples were used to average each set of experimental data. EDS and XRD analysis were performed to identify the interfacial phase on the fracture surfaces. The brazed specimens for XRD analysis were prepared by shear strength test. Then, the prepared specimens were polished layer by layer along the direction parallel to the brazing seam. Therefore, The XRD analysis can be executed on the surface of TC17 side.

![Figure 2](image_url) Schematic diagrams of (a) brazing assembly and (b) shear test experiment

3. Result and Discussion

3.1. Typical Interfacial Microstructure of TC17/AgCuTi/C/C Composite Joints

In this study reliable brazing of C/C composite and TC17 alloy was achieved using Ag-Cu-Ti foil. Figure 3 shows the typical interfacial microstructure and the main element of C/C composite and TC17 joint brazed at 860°C for 15min. Figure 3(a) clearly presents that the interface are free of microcracks and pores and the joint exhibits sound bonding. The joint consists of one diffusion layer and three reaction layers, as shown in figure 3 (a): zone I (diffusion layer adjacent to TC17 alloy), zone II (reaction zone adjacent to diffusion layer), zone III (brazing seam) and zone IV (continuous thin reaction layer adjacent to C/C composite).

| Table 1. | Ti  | Cu  | Ag | C  | Possible Phase       |
|----------|-----|-----|----|----|----------------------|
| A        | 93.29 | 6.41 | 0.3 |  | Diffusion layer       |
| B        | 67.96 | 29.91 |2.14 |  | Ti$_2$Cu              |
| C        | 51.32 | 45.86 | 2.82 |  | TiCu                 |
| D        | 4.22  | 7.42  |88.36 |  | Ag(s, s)             |
| E        | 42.01 | 48.81 | 9.18 |  | Ti$_3$Cu$_4$          |
| F        | 42.73 | 54.67 | 2.6  |  | Ti$_3$Cu$_4$          |
| G        | 44.76 | 52.81 | 2.43 |  | TiCu                 |
| H        | 26.93 | 1.35  |5.26 |66.46 | TiC                  |
Figure 3 (b) and (c) show the magnified microstructures of TC17/AgCuTi interface and AgCuTi/C/C composite interface, respectively. It can be seen that there exist one thin layer (layer H) near C/C composite side and three reaction layers (Layer B, C and F) near TC17 side. In the center of brazing zone, there are three different phases: gray phase (marked by F), white matrix phase (marked by D) and dark block phase (marked by G). The EDS result of A-H zones were listed in Table 1.

Figure 3. Back-scattered electron image of C/C composite/AgCuTi/TC17 joint (a) the brazed joint at 860°C for 15min, (b) AgCuTi/TC17 interface, and (c) C/C composite/AgCuTi interface (d) interface between C/C composite and interlayer and EDS element distribution maps of Ti (e) EDS element distribution maps of Cu (f) EDS element distribution maps of Ag

According to the EDS result and Ti-Cu binary alloy diagram[17], the three reaction layers in zone II are probably Ti2Cu (layer B), TiCu (layer C) and Ti3Cu4 intermetallic phase (layer F). The content of element Ti and Cu indicates that diffusion and reactions occur between base material and brazing filler. Along layer A, layer B, layer C, and layer F, the content of element Ti decreases while the element of Cu increases gradually. This indicates that diffusion and reactions between base material and brazing filler. In the center of brazing zone, the white phase (marked by D) is Ag-based solid solution (abbreviated as Ag(s,s)) while the dark phase (marked by G) and gray phase (marked by E) are probably TiCu and Ti3Cu4. Moreover, the layer H is very thin and mainly composed of Ti (~26.93 at.%) and C (~66.46 at.%). The content of C element in layer H is higher than other layer. One reason is that
C element from the C/C composite diffused into layer H during brazing process. According to the thermodynamic data manual [18], the Gibbs free energy of TiC formation are represented as follows:

$$\Delta G^0(\text{KJ/mol}) = -183.1 + 0.01T$$

The Gibbs free energy of forming TiC calculated by Formula (1) is about -172 KJ/mol at 860°C. The Gibbs free energy of forming TiC is negative. Therefore, element Ti and C can react with each other at 860°C. The formation of TiC promotes the wettability of brazing filler on C/C composite, which is in accordance with literatures reported by other researchers [19]. According to Ag-Cu binary alloy phase diagram [17], during the brazing process, the AgCu eutectic melt firstly, and then the element Ti can dissolve in it. The dissolved Ti diffused toward to C/C composite, and finally reacted with the element C to form TiC reaction layer.

To further identify the phase constitutions, XRD analysis for C/C composite/TC17 brazed joint is performed. Figure 4(a) shows the XRD pattern of the surface of joint brazed at 860°C for 15 min after shear tests. The peaks of TiC phase could be indexed in the profile. Figure 4(b) shows the XRD pattern of the surface of joint brazed near to diffusion layer after polishing process. The peaks of Ti$_2$Cu phase can only be indexed in Figure 4(b). It is indicated that Ti$_2$Cu is only formed near TC17 alloy side. This is accordance with the EDS result. Cu(s,s) is indexed in Figure 4. According to EDS result, Cu(s,s) cannot be identified accurately from layer A to F. In accordance with literatures reported by other researchers on brazing carbon materials [4, 14, 19], Cu(s,s) probably exists in layer G and/or layer E. As analyzed above, the typical interfacial microstructure of brazed joint is TC17/diffusion layer/Ti$_2$Cu+TiCu+Ti$_3$Cu$_4$/Ag(s,s)+Cu(s,s)+TiCu/TiC/C/C composite.

Figure 4. XRD pattern from the surface of joint brazed at 860°C for 15 min after shear tests (a) layers at TC17 side (b) layers near to diffusion layer after polishing process.
3.2. Effect of Brazing Temperature on the Interfacial Microstructure of TC17 /AgCuTi/ C/C Composite Joints

Figure 5 illustrates the interfacial microstructures of TC17 /AgCuTi/ C/C composite joints brazed at 840°C, 880°C, 900°C and 920°C, for 15 min. It can be seen the interfacial microstructure has significantly changed with the increase of brazing temperature from 840 to 920°C. Because of the effect of capillarity at high temperature, the molten filler is expelled out of the joint gap. Therefore, the width of brazing seam decreases with the increasing temperature. On the contrary, the increasing temperature is beneficial to the intensive diffusion and dissolution between brazing filler and TC17 alloy. So the thickness of diffusion increases with the increasing temperature. On the other hand, Ti$_2$Cu and TiCu layers close to TC17 side thicken gradually with the increasing temperature. However, Ti$_3$Cu$_4$ layer firstly thickens when the brazing temperature is blow 900°C and decreases significantly when the temperature exceeds 900°C as shown in Figure 5.

According to the literature [16], it can be explained that when the temperature reaches 920°C, the excessive growth of TiCu phase in the brazing seam which depletes element Ti and Cu. Therefore, Ti$_3$Cu$_4$ layer almost disappears. High magnified SEM image of TiC layer was obtained (the inserted images in Figure 5) to investigate the thickness of TiC layer changes when the brazing temperature increases. With the increasing temperature, the TiC layer thickens gradually. The TiC layer is thin at lower brazing temperature (840°C). Further increasing the brazing temperature to 900°C and 920°C, as shown in Figure 5(c) and (d), the formation of massive TiC layer is detected which deteriorates the property of brazed joint.

With the increase of temperature from 840°C to 920°C, Ag(s,s) phase changes obviously. When the brazing temperature reaches to 920°C, Ag(s,s) phase changes into a integrated layer. According to the literature [20], the Ag-Ti system exhibits a weak compound formation tendency compared to the Cu-Ti system. Because of the effect of high temperature, the content of TiCu increases obviously.
3.3. Mechanical Property Evaluation of the TC17/AgCuTi/C/C Composite Joints

The effect of the brazing temperature on the shear strength of the joints is shown in Figure 6. When the brazing temperature is relatively low (840°C), the reaction at brazing joint is insufficient and the diffusion layer is very thin. Thus, the shear strength of the joint is lower. As the brazing temperature increases, the reaction at brazing joint increases greatly and the shear temperature increases as well. When the brazing temperature is 860°C, the shear strength reaches a maximum of about 24 MPa. Further increasing the brazing temperature, the shear strength of joints is stabilized (about 23 MPa). When the brazing temperature reaches 900°C and 920°C, the shear strength of joints decreases significantly.

4. Conclusion

Brazing of C/C composite to TC17 alloy was performed at 840, 860, 880, 900 and 920°C for 15 min by using AgCuTi brazing filler alloy. The interfacial microstructure and effects of brazing temperature and mechanical property of brazed joints are investigated in this study. The main findings are summarized as follows.

1) The TC17 alloy and C/C composites are successfully joined with Ag-Cu-Ti active filler metal by vacuum brazing.
2) The typical interfacial microstructure of the brazed joint is TC17/diffusion layer/Ti2Cu+TiCu+Ti3Cu/Ag(s,s)+Cu(s,s)+TiCu/TiC/C/C composite.
3) With the increase of brazed temperature, the thickness of diffusion layer, Ti2Cu layer, TiCu layer and TiC layer increase and the width of brazing seam decreases gradually respectively.
4) The maximum shear strength of the joint is 24±1 MPa brazed at 860°C for 15 min.

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6. References

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