Microstructure evolution and mechanical properties of vacuum-brazed C/C composite with AgCuTi foil

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The microstructure and bonding strength of vacuum-brazed C/C composite and C/C composite with AgCuTi foil are studied. The interface structure of the brazed joint is C/C composite–TiC–eutectic structure of AgCu–TiC–C/C composite. The maximum shear strength of the joint is about 20 MPa and TiC formed at the edge of C/C composite plays a key role in the brazing process. It improves the wettability of the C/C composite and inhibits diffusion of the Ag and Cu atoms in the filler metal and C atoms in the C/C composite. The fracture mode of the brazing joint is brittle. The interface evolution in the brazing process and associated mechanism are discussed.

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1. Introduction

Carbon/carbon (C/C) composites are attractive materials in thermo-structural applications due to the low density, small coefficient of thermal expansion (CTE), high thermal conductivity (better than copper and silver), and especially excellent high-temperature mechanical and thermal shock resistance (high strength and toughness can be maintained up to more than 3000 K). C/C composites have thus been in high temperature applications including hypersonic aircraft thermal structures, high thrust–weight ratio turbine engines, rocket nozzles, space shuttles, and nuclear reactors\cite{1,2}. However, being an intrinsic brittle ceramic, it is difficult to fabricate C/C composites into components with a complex shape by conventional methods thereby hampering wider utilization of the materials. One of the possible solutions is to employ joining technology.

Several joining techniques have been developed for joining C/C composites, and diffusion bonding, reaction forming\cite{3,4}, and brazing\cite{5–16} appear to be the most attractive methods. Since diffusion bonding requires a high bonding temperature up to 1700 °C, loading pressure, and high-quality matching bonding surface, the use of this technique tends to be limited. C/C composites can be joined by reaction forming using Ti–Si–C at 1823 K, and the transition interlayer is prepared at an even high temperature of 2073–2273 K\cite{3}. Milena Salvo has tried some possible filler materials, such as Si sheet, aluminum sheet, titanium powder, titanium sheet, Mg\textsubscript{2}Si powder, SB-glass powder and ZBM-glass powder, to join C/C composites, and the joint with Si sheet filler material brazed at 1693 K for 90 min shows best shear strength at room temperature. The average shear strength of the joints is 22 MPa\cite{4}. The high bonding temperature limits the use of diffusion bonding and reaction methods. In comparison, vacuum brazing is a more effective process due to its simplicity, low cost, mass production capability, and widespread applications. Active brazing is a conventional method to join ceramic materials to metals and applicable to C/C composites\cite{5–16}. Brazing of C/C composite to other metals with reactive fillers has been performed by others\cite{7,8,11,12,15}. Ag based filler metals such as TiCuSi or Copper ABA have been used because of the fact that a higher strength is obtained with Ag based filler metals than Ni- and Ti-based filler metals\cite{17}. Moreover, the brazing mechanism and related interfacial reactions between the carbon system (mainly graphite and diamond) and metal has been proposed by Eustathopoulos et al.\cite{18}. In their work, reactive fillers including Ti or Cr were used to join carbon materials (graphite, diamond and C/C composite). However, C/C composite is made of carbon fibers with complicated microstructures, and the joining technology must be further explored. In addition, the microstructure evolution and strength of the joints in the brazing process need more in-depth and systematic studies. Furthermore,
the metallurgical reaction in the joining interface during the brazing process is needed further researched and discussed.

The differential CTEs of the joining materials likely create thermal stress during the brazing process and the absence of thermal stress in the bonding interface reduces the strength of the joint. Past work tends to focus on the thermal stress in the brazing joint between the C/C composite and other materials [13]. Several measures such as drilling, wave interface [13], stress relief interlayer [11,16], and so on have been taken to accommodate the thermal stress. However, the thermal stress problem associated with C/C composite and C/C composite joint has seldom been investigated. It should be noted that the filler alloy has much larger CTE than the C/C composite and the mismatch between the CTE of the C/C composite and filler alloy also creates thermal stress in the joining interface during the brazing cooling process. Hence, fractures across the interface or big holes likely form at the interface if the filler alloy has poor ductility.

In this study, the microstructures of C/C composite and C/C composite brazed joints with AgCuTi filler are investigated. The interface evolution is analyzed and mechanical properties of the joints are also determined.

2. Experimental details

The semi-3D (three-dimensional) C/C composite was fabricated by needled felt and carbon fiber cloth. The C fiber was 99.9 wt% pure 12 K acrylic-based activated materials. The three-point flexural strength was about 80–100 MPa, shear strength was about 30–40 MPa at room temperature. A density of 1.6–1.7 g/cm³ and residual porosity of 10–20% were obtained. The microstructure of the C/C composite is shown in Fig. 1.

A commercial foil of Ag–27Cu–3.5Ti (wt% nominal composition) with a thickness of about 50 μm was used, and its solidus and liquidus temperatures were about 780 °C and 900 °C. The C/C composite samples were cut into 10 mm × 5 mm × 5 mm rectangular blocks using a wire-cutting machine prior to brazing. The joining surfaces were ground by 1000 grit silicon carbide paper and then cleaned ultrasonically with ethanol. The AgCuTi brazing foil was sandwiched between the C/C composite samples and a special jig was used to maintain good contact between the joining surfaces. The brazing experiments were carried out in a vacuum furnace controlled to ±1 °C between 850 °C and 940 °C. Brazing was conducted for 5–60 min at a pressure of less than 5 × 10⁻³ Pa vacuum degree. The brazing temperature–time curve is depicted in Fig. 2.

After brazing, the joints were mounted and polished for microstructure evaluation. The microstructure was examined on a scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) and the phase composition was determined by X-ray diffraction (XRD). The shear strength of the joints was investigated using the GLEEBLE-1500 thermomechanical simulator machine at room temperature and the fracture characteristics were also evaluated. The schematic of the shear test is shown in Fig. 3.

3. Results and discussion

Fig. 4 presents the microstructures of the joints brazed at 880, 900, 910, and 940 °C for 10 min and those of the joints brazed at 900 °C for 5, 10, 30, and 60 min are displayed in Fig. 5.

Past results show that the CTE of C/C composites is about 0–1.0 × 10⁻⁶ K⁻¹ in the range of 20–250 °C, and 2.0–4.0 × 10⁻⁶ K⁻¹ from 250 to 2500 °C [19]. However, the CTE of the Ag–Cu–Ti filler (about 18–20 × 10⁻⁶ K⁻¹) is much larger than that of the C/C composite. The mismatch in the CTE between the C/C composite and filler results in larger thermal stress at the joining interface during the brazing process. However, the small thickness and good plastic deformation ability of the AgCuTi foil help to accommodate the thermal stress. According to the macrostructure of the joint, there are no big holes or fractures at the interface of the entire joint. Based on the SEM micrographs (Figs. 4 and 5),
the interface is joined well and conventional defects such as cracks and holes are not observed. The widths of the brazed joints vary from 10 μm to 50 μm. The C/C composites possess intrinsic micro-cracks and pores, and the filler metal infiltrates into the C/C composites along these micro-gaps, as shown in Figs. 4 and 5. It should be noted that the intrinsic cracks are beneficial to the fatigue properties of C/C composites.

To evaluate the phase composition of the interface, XRD is conducted on the fracture surfaces of joints produced at 880 °C, 900 °C, 910 °C and 940 °C for 10 min and the results are given...
in Fig. 6. The interface consists of TiC, Cu(S.S), Ag(S.S), and C phases. The filler metal is composed of Ag, Cu, Ti and C/C composite is made of C, thereby constituting a metallurgical system comprising Ag, Cu, Ti, and C. It is well known that Ag–Cu is a segregating system, immiscible in the solid state, and a single phase in liquid. The eutectic temperature of the materials with 28 wt% Cu is about 780°C. Introduction of Ti to the Ag–Cu eutectic system changes the system energetic. It has been shown that Ti and Cu have negative values of the Gibbs energy of mixing and can form a series of intermetallic compounds such as CuTi2, CuTi, Cu4Ti3, Cu3Ti2, Cu2Ti, Cu4Ti, etc. or CuTi in the general term at the brazing temperature [20]. However, only two intermetallic compounds, AgTi and Ag3Ti (termed AgTi) from the Ag–Ti binary phase diagrams [21] exist in the Ag–Ti binary system at high temperature. The mutual exclusion between Ag and Ti, Cu and Ti is important. It has been shown that the partial enthalpy of the Ti solution in molten Cu at infinite dilution is −10 kJ/mol, whereas it is 39 kJ/mol in Ag [22]. Hence, the Ag–Ti system has a weak compound formation tendency compared to the Cu–Ti system. Many intermetallics of CuTi come into being during the brazing temperature (below 940°C) when the AgCuTi filler is used to join C/C composites and TC4 [14]. However, XRD does not reveal intermetallic phases such as TiCu, Ti2Cu, Ti2Cu, etc., nor intermetallic compositions of Ag and Ti in C/C composite and C/C composite joint with AgCuTi.

The Gibbs free energy formation of TiC (Ti+C → TiC) is negative. It is from −174 to −169 kJ between 920 and 1050°C [19], and so formation of Ti and C is thermodynamically possible at the brazing temperature. On the other hand, the absence of CuTi shows that TiC forms more easily than CuTi intermetallics compounds. Furthermore, Cu3Ti2 compounds produced during the brazing process are changed by the following reactions [23]:

$$\text{Cu}_3\text{Ti}_2 + y\text{C} \rightarrow y\text{TiC} + x\text{Cu}$$

In this metallurgical system, Ti content is small (about 3.5 wt%). Therefore, the reaction between C and Ti occurs adequately due to diffusion of Ti in the liquid Ag–Cu alloy to the edge of the C/C composite. Most of the Ti is exhausted by C and hence, CuTi and AgTi cannot be detected by XRD.

To further study metallurgical reaction at the interface between the C/C composite and AgCuTi, a high-magnification figure is presented in Fig. 7. A clear layered structure is formed in the joint and EDS is performed at different regions. In zone I, flakes with a thickness of 0.5 μm form between the AgCuTi filler and C/C composite. The composition is 15.58 wt% Ti, 77.77 wt% C, 1.93 wt% Ag, and 4.72 wt% Cu constituting a phase of TiC + Cu(S.S). It is noted that TiC phase formation is the key to the joint formation, which leads to better wettability on the AgCuTi filler [24]. The gray zone in the joint is Cu rich (Cu (S.S)) and the white zone is Ag rich (Ag (S.S)), denoted in Fig. 7.

The reaction between Ti and C is not limited to the interface between the AgCuTi and C/C composite and it can be seen that
some fillers infiltrate along the micro-gaps into the C/C composite. Similar microstructures [Ti aggregated (TiC Formation)] are produced in the infiltration filler gaps near the C/C composite interface (zone II in Fig. 7). The infiltration increases the strength of the joint by enlarging the joint area and avoiding stress concentration.

To evaluate elemental diffusion at the interface of the joint, line scans and elemental maps are obtained by EDS across the joining zone and the results are depicted in Figs. 8 and 9. The line scans reveal the presence of Ti, Cu, Ag, and C, and Ti aggregates at the edge of the C/C composite. Similar results are shown by the elemental maps (Fig. 9). Adjacent to the Ti aggregation (TiC) besides the C/C composite (Ti wave crest in Fig. 8), Cu aggregation and Ag aggregation zone (eutectic microstructure of Ag and Cu) is observed. It is interesting that Cu and Ag are distributed alternately in the bonding zone. Another phenomenon observed from Fig. 8 is that Ag and Cu exist in the Ti wave crests but most of C is outside. Literature shows that if TiC is compact enough, not only Ag and Cu elements but also small atom C element [25], cannot diffuse through it due to their lower diffusion ability in TiC.

Based on the data, an interface evolution model is proposed and illustrated in Fig. 10. It comprises the following stages:

1. **Physical contact with rising temperature**: In this stage, the filler deforms plastically under the load and makes physical contact as the brazing temperature is increased.

2. **Diffusion of atom**: Here, atom diffusion increases with increasing temperature. Ti atom diffuses from the filler metal to C/C composite interface, as shown in Fig. 10a. However, the diffusion rates are small when the temperature is low.

3. **Further diffusion and interface reaction**: Diffusion continues and increases with the temperature raising. The reaction between Ti and C has occurred at the interface of C/C side and TiC has been produced before the filler melts completely [26], as illustrated in Fig. 10b. In this stage, the reaction proceeds faster as the temperature goes up.

4. **Growth of reaction layers**: The TiC thickness increases with brazing temperature and holding time. Since TiC layer is thin and discontinuous, C can diffuse through it even at a low brazing temperature and short holding time, and react with Ti diffused from filler metal. As TiC layer forms continuously as the temperature and holding time are raised, the thickness of

![Fig. 8. EDS line scan of the joint.](image)

![Fig. 9. EDS elemental maps of the joint: (a) Scanning position, (b) Cu, (c) Ag, (d) C, and (e) Ti.](image)
the TiC layer increases, shown in Fig. 10c. Furthermore, TiC layer becomes more compact gradually and so diffusion of C from C/C to filler metal through TiC becomes more difficult.

(5) Freezing of reaction layers and formation of the eutectic structure of silver, copper: TiC exists in the solid state when the temperature is above the melting point of the filler metal due to its high melting point. When the temperature begins to drop, the filler metal begins to freeze and the eutectic structure of silver and copper forms when the brazing temperature dips below the freezing point of the filler metal, as shown in Fig. 10c. Finally, the interfacial structure composed of C/C composite – TiC–eutectic structure (AgCu)–TiC–C/C composite forms.

The effects of brazing temperature and holding time on the shear strength of the joints are shown in Fig. 11, and each data point is obtained by averaging three measurements. When the brazing temperature is $850 \, ^\circ\text{C}$, the shear strength of the joint is lower (about $15.5 \, \text{MPa}$). It is because the atomic energy is smaller at a low temperature and the interlayer reaction between the filler alloy and C/C composite is insufficient. As the temperature goes up, the atom energy increases and diffusion is enhanced leading to faster interface reactions especially after the filler metal melts. Fig. 11b reveals that when the holding time is 5 min (short), the shear strength of the joint is about $11 \, \text{MPa}$. Both element diffusion and interface reactions take time and 5 min is too short. When the holding time is increased, more diffusion and reactions occur and higher shear strength results. When the brazing temperature is $900 \, ^\circ\text{C}$ and holding time is 10 min, the shear strength reaches the maximum value of about $20 \, \text{MPa}$. However, further increase of the brazing temperature and holding time reduces the shear strength due to formation of much more brittle intermetallics in the interlayer. For instance, when the brazing temperature is raised to $940 \, ^\circ\text{C}$ for 10 min, the shear strength declines to $12.1 \, \text{MPa}$. If the holding time is prolonged to 90 min ($900 \, ^\circ\text{C}$), the shear strength is about $15.4 \, \text{MPa}$.

The typical fracture microstructures of the brazed joint are shown in Fig. 12 and a brittle fracture mode is disclosed. Three types of fracture morphologies are present in the different zones on the fracture surface (denoted as A, B, C in Fig. 12a) due to different distributions of carbon fibers, namely perpendicular, parallel, and oblique (transition zone) to the fracture surface. Fig. 11b, c, d shows the magnified microstructures of the three types, correspondingly. Fig. 12b shows the microstructure in zone A and a white interlayer observed above the circular carbon fibers. Fig. 12c shows the fracture morphology in zone B and Fig. 12d is that of the transition zone in the joint. It can be observed that the crack propagates along the TiC and eutectic structure of AgCu.

4. Conclusion

The microstructure and bonding strength of vacuum-brazed C/C composite and C/C composite with AgCuTi foil are experimentally studied at $850–940 \, ^\circ\text{C}$ for holding time between 5 and 60 min. The maximum shear strength of the joint is about $20 \, \text{MPa}$.
achieved at 900 °C and 10 min. The interface structure is C/C composite–TiC–eutectic structure of AgCu–TiC–C/C composite. TiC forming at the edge of the C/C composite plays a key role in the brazing process by improving the wettability of the C/C composite and inhibiting diffusion of Ag and Cu atoms in the filler metal and C in the C/C composite through it. The fracture mode of the brazed joint is observed to be brittle. The interface evolution comprises of the following 5 stages: (1) physical contact with increasing temperature, (2) diffusion of atom, (3) further diffusion and interface reaction, (4) growth of the reaction layers, and (5) freezing of reaction layers and formation of the silver–copper eutectic structure.

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