The Microstructure and Shear Strength of SiC Joints Brazed with SiC Particle Reinforced Si-24Ti Alloy

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Abstract. To refine the microstructure and increase the joint strength of SiC ceramic brazed with Si-24Ti (wt.%), carbon nanotubes (CNT) were added into Si-24Ti brazing alloy to form SiC particles in the braze zone. The effect of the amount of CNT in the brazing alloy on the microstructure and shear strength of joints was investigated. The microstructure and element distribution of the joint was studied by scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS). The results indicated that the addition of the proper amount (1-3 wt.%) of CNT could refine the microstructure of joints and achieve high-quality SiC joints. The shear strength of the joint brazed with 3 wt.% CNT addition reached the maximum value of 108 MPa, which was 21.3% higher than that of without CNT (89 MPa). However, when the amount of CNT increased to 5 wt.%, the shear strength of joint decreased to 55 MPa, due to the formation of cavity in the joint. The strengthening mechanism of in-situ formed SiC particle in the composite brazing alloy was evaluated.

1. Introduction

SiC ceramic and its composites are widely used in the nuclear industry, chemical industry, military and metallurgical due to its advantages of excellent anti-neutron swelling ability, satisfactory radiation resistance, higher strength and splendid hardness[1]. However, because of the brittleness and high hardness of SiC ceramics, it is difficult to directly form or process components with complex shapes and large sizes, hence SiC ceramic joining technology is very important for its engineering application. At present, the major joining technologies of SiC ceramics are brazing [2], diffusion bonding [3] and transient liquid phase bonding [4]. Higher pressure may cause the mechanical properties degradation for the fiber reinforced composites. Also, because the surface roughness requirement is not as rigorous as that for diffusion bonding, the process of brazing is relatively simple. As a result, brazing is one of the key technologies to for joining of ceramics [5].

The high-temperature properties of SiC ceramics have received unprecedented attention in some specific industries. To maximize the excellent high-temperature properties of the brazed SiC ceramic joint, it is necessary to select brazing filler metal with a high melting point. Li et al. [6] used 22Ti-78Si (wt%) high-temperature eutectic alloy fabricated by non-consumable arc melting technology for joining of SiC ceramic. The shear strength of the SiC/Si-22Ti/SiC brazed joint reached 125 MPa, when brazing temperature was 1400°C, holding time was 10 min and brazing zone thickness was 100 μm. To improve the strength of joints, researchers have done a lot of work on the mismatch of thermal expansion coefficient and elastic modulus between the base metal and intermediate layer. Wen et al. [7]to solve the problem of expansion coefficient mismatch of SiC/Si-24Ti/SiC joint, SiC ceramics
were brazed with SiC particle reinforced Si-24Ti eutectic filler metal. The experimental results showed that the effect of adding SiC particles significantly refined the size of coarse TiSi$_2$ phase, which improved the shear strength of the joint. Microstructure refinement in the joint have also been reported by Zhao et al. [8] who brazed Si3N4 to TC4 alloy with Si3N4 particulate-reinforced Ag-Cu alloys. M.C. Halbig et al. [9] also studied in detail the microstructure of the joint brazed with Ag-Cu-Ti alloy containing with different amount of SiC particulates to control the microstructure and to enhance the joint strength. In recent years, carbon nanotubes (CNT) as reinforcing materials have shown excellent properties in titanium matrix composites. Recently, Song et al. [10] joined C/C composites and Ti6Al4V alloys with TiCuCrNi alloy reinforced by CNT, and the results showed that CNT had a great influence on the microstructures and mechanical properties of the joints.

In this work, to explore a more suitable high-temperature brazing technology, CNT was added into Si-24Ti near eutectic brazing alloy to form SiC particles in the braze zone. Based on the previous studies, the eutectic reaction in the Si-24Ti phase diagram happened at 1330 $^\circ$C, the melting point of Si-24Ti alloy is about 1327 $^\circ$C [7]. In this experiment, the brazing temperature was set to be 1380$^\circ$C. The effects of CNT content on the microstructure and mechanical properties of joints were studied, and the strengthening mechanism of SiC particle in the composite brazing alloy was evaluated.

2. Experimental

The SiC ceramics used in this experiment (Shandong Jinde New Material Company, China) had been machined into 15 mm $\times$ 15 mm $\times$ 4 mm specimens by a diamond cutting machine. The specimens were polished by an automatic precision grinding polishing machine using a diamond abrasive fluid with a diameter of 3 and 1 $\mu$m. High purity silicon (>99.9%) and sponge titanium (>99.5%) were proportioned according to the mass ratio of 76:24, and then Si-24Ti eutectic alloy was melted by non-consumable arc melting technology in high vacuum environment. The melted alloys were crushed mechanically, and then the crushed near-eutectic alloys were ground into powders with a particle size of less than 1 mm, and then the powders were ground into Si-24Ti eutectic alloys with an average particle size of 20 $\mu$m by ball milling. The diameter and length of CNT reinforced particles are 8-15 nm and 10-50 $\mu$m, respectively. The CNT powder with mass fractions of 0 wt.%, 1 wt.%, 3 wt.% and 5 wt.% was mixed with alloy powder. The weighed powder was put into a beaker and poured into a certain amount of alcohol. At the same time, it was mechanically stirred and ultrasonic dispersed. Then the mixed powder was dried at 30 $^\circ$C for 24 hours, and then screened.

Under the conditions of brazing temperature 1380$^\circ$C, holding time 20 min and heating speed 10$^\circ$C /min, brazing experiments were carried out in a vacuum furnace, and the samples of brazed joints were obtained. The microstructure and element distribution of the joint were investigated by scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS). The shear strength of the joint was tested on a universal testing machine with a loading speed of 0.5 mm/min for the sample size of 3 mm $\times$3 mm $\times$ 8 mm. In this study, the shear strength of SiC brazed joints was tested by four shear test samples, and the average value was obtained. The morphology of shear fracture was observed by SEM.

3. Results and discussion

3.1. Microstructural characterization

Figure 1 (a) is a SEM backscatter image of SiC/Si-24Ti-3CNT/SiC brazed joint brazed at temperature of 1380$^\circ$C and with a holding time of 20 min. It can be seen that the interface of the joint is well-bonded, continuous and crack-free. The braze zone mainly consists of the gray phase, the white phase, and the black phase. Table 1 gives the element contents for the points 1, 2 and 3 in Figure 1 (a). One can be seen from Table 1, point 1 (Si: 52.04 at.%, C: 47.96 at.%) may be the SiC phase, point 2 (Si: 66.94 at.%, Ti: 33.06 at.%) may be the TiSi$_2$ phase, and point 3 (Si: 99.63 at.%, Ti: 0.37 at.%) may be the Si phase(a small amount of Ti element diffused during brazing process). The SiC phase observed in the brazing zone is mainly due to the chemical reaction between the silicon element of Si-24Ti alloy and CNT during brazing, the chemical reaction may be as following:
Si + [CNT] \rightarrow \text{SiC} \quad \text{(1)}

\text{TiSi}_2 + [\text{CNT}] \rightarrow \text{SiC} + \text{Ti} \quad \text{(2)}

\text{TiSi}_2 + [\text{CNT}] \rightarrow \text{SiC} + \text{TiSi} \quad \text{(3)}

Figure 1. Backscattered SEM images of the joint brazed with Si-24Ti -3CNT.

Table 1 Element contents of points 1, 2 and 3 in Figure 1.

| Point | Si(at.%) | Ti(at.%) | C(at.%) |
|-------|----------|----------|---------|
| 1     | 52.04    | -        | 47.96   |
| 2     | 99.63    | 0.37     | -       |
| 3     | 66.94    | 33.06    | -       |

From Figure 2(a), the Si phase and coarse TiSi$_2$ phase could be seen in the joint. The contact area between the coarse TiSi$_2$ phase and SiC base matrix is larger, which may reduce the mechanical properties of the joint because of the large difference in the coefficient of thermal expansion (CET) between the two phases. By the increasing of CNT content, the interlayer structure of joints was refined gradually as Figure 2(b)-(d), and the volume fraction of the Si+TiSi$_2$ eutectic zone in the interlayer increases. From Figure 2(a), (b) and (c), micro-cracks mainly occurred in the coarse TiSi$_2$ phase, the white arrow indicated the location of micro-cracks in the brazing zone. The main reason may be that the CET of TiSi$_2$(9×10$^{-6}$/K) is quite different from Si(2.5×10$^{-6}$/K) and SiC(4.35×10$^{-6}$/K) [7]. Residual stress is easy to occur during the brazing cooling process, thus micro-cracks formed in the joints. Besides, because TiSi$_2$ itself has the characteristics of brittle, which also lead to micro-cracks occur in the TiSi$_2$ phase.

By changing the microstructure of brazing alloy, in adding fine ceramic particles in the brazing zone is a common method for improving the mechanical properties of brazing alloy [11]. From Figure 2, the coarse TiSi$_2$ phase refined gradually by adding an appropriate amount of CNT. SiC phase and Si+TiSi$_2$ eutectic zone were also observed in the brazing zone. The reasons for the above experimental results may be as follows: there is a chemical reaction between Si-24Ti eutectic and CNT occurs during the brazing process, which results in initial grain refinement. Also, it is well known that the small size secondary phase with uniform grain boundary distribution has a strong pinning effect on grain boundary migration, which is an obstacle to grain growth[12]. SiC particles generated in-situ
disperse in the brazing zone, forming multiple nucleation particles during the brazing cooling stage, inhibiting the growth of the TiSi$_2$ phase and further refining the grains. However, when 5 wt.% CNT was added to the composite filler metal, pores appear in the brazing zone of SiC/SiC joint. From Figure 3(d), agglomerated SiC particles (5 μm) were observed around the cavity. The results show that adding too much CNT will react violently with Si-24Ti eutectic and produce much SiC particles in the brazing zone, resulting in poor fluidity and wettability of the brazing alloy, which may make the pores to occur in the brazing process. In this situation, higher brazing temperature is needed to eliminate the cavity in the joints, because higher temperature can improve the fluidity of the filler metal [13].

Figure 2. SEM-BSE images of SiC joints brazed with Si-24Ti-0CNT, Si-24Ti-1CNT, Si-24Ti-3CNT, and Si-24Ti-5CNT. (a) Si-24Ti-0CNT joint, (b) Si-24Ti-1CNT joint, (c) Si-24Ti-3CNT joint, and (d) Si-24Ti-5CNT joint.

Figure 3 (a) is a high magnification SEM-BSE image of the joints brazed with Si-24Ti-3CNT. It can be seen that the bonding interface is well bonded. Random distribution of in-situ formed SiC, TiSi2 and Si in the brazing zone. According to the EDS analysis(Figure 3(b)), Ti is mainly enriched in TiSi$_2$, while Si is mainly enriched in Si solid solution, C is mainly enriched in SiC matrix and in-situ formed SiC. This further indicates that chemical reaction occurs in the brazing zone and SiC is formed in-situ because of the addition of CNT in the composite filler metal. The position shown by the purple arrow in Figure 3 (b), it can be seen that at the interface of the two phases of Si and TiSi$_2$, the element distribution shows that the content of Ti increases gradually, the content of Si decreases gradually, and Ti element is also detected in the Si phase. The main reason for the above results was that the diffusion of elements occurred during brazing, and the diffusion ability of elements is inversely proportional to the distance. Ti element is enriched in TiSi$_2$, so the peak of the Ti element detected is lower when it is
farther away from the TiSi₂ phase, therefore there would be an upward trend when the Ti element peak reaches TiSi₂ phase. Similarly, it could be seen that the peak of the Si element would have a downward trend when it reaches the TiSi₂ phase.

**Figure 3.** (a) SEM-BSE image of SiC joints brazed with Si-24Ti-3CNT and (b) EDS line-scanning of elements distribution.

![Figure 3](image)

**Figure 4.** The shear strength of brazing zone of SiC joints brazed with different CNT content in brazing fillers.

![Figure 4](image)

3.2. Mechanical properties evaluation

The results of Figure 4 showed that the shear strength of the SiC brazing joint is related to the content of CNT in composite brazing filler metal. The shear strength of Si-24Ti-0CNT joints are relatively low, 89MPa. With the increase of CNT content in the composite brazing alloy, the shear strength of the SiC joint increases gradually. Until joining 3wt.% CNT, the maximum shear strength of the SiC joint reaches 108 MPa, which is 21.3% higher than that of the Si-24Ti-0CNT joint. However, when 5 wt.% SiC particles were added, the shear strength of the joint dramatically decreased to 55 MPa. These phenomena can be explained based on the second-phase dispersion strengthening principle. The mechanical properties of the composite interlayer can be improved by introducing the hard-reinforcement phase SiC in-situ through a chemical reaction [10,11]. The in-situ formed reinforcement SiC can also be used as a nucleation particle, which inhibits the growth of the TiSi₂ phase and refines
the joint, which makes the shear strength of SiC brazed joint increase. However, when excessive CNT was added, CNT reacted with Si-24Ti and consumed too much liquid phase in the composite brazing alloy, and produced excessive SiC particles in the brazing zone, resulting in poor fluidity and wettability of the intermediate layer, which makes it easy to produce pores in the brazing process and reduces the shear strength of the joints.

3.3. Fracture morphology and strengthening mechanism of CNT in composite brazing alloy

Figure 5(a) is the SEM-BSE images of fracture surfaces of the Si-24Ti-3CNT joint. After the shear test, one can see most of the fracture surface areas were broken in the middle layer, and only a few of them were broken on the base material of SiC. The main reason for this result is that the addition of carbon nanotubes in the composite brazing alloy can improve the microstructure of the joint. Based on the mechanism of fine grain-strengthening, SiC particles formed by the in-situ reaction can be used as nucleation particles to inhibit the coarsening of TiSi2. Moreover, SiC particles formed by in-situ reaction have almost no difference in the thermal expansion coefficient from the SiC base matrix, which greatly reduces the thermal expansion coefficient of the whole brazing alloy and effectively alleviates the generation of residual stress.

![Figure 5](image)

**Figure 5.** SEM-BSE images of fracture surfaces of (a)SiTi-3CNT joint,(b) crack propagation behavior around SiC formed by in-situ reaction.

The strengthening mechanism of CNT particles in composite filler metals can be attributed to two main points: firstly, fine TiSi2 phase and a large amount of Si+TiSi2 eutectic zone were obtained by refining the joint structure; secondly, SiC phase is in-situ formed in the brazing zone, and SiC phase plays a role of particle dispersion enhancement. Figure 5 (b) is an in-situ crack propagation behavior near SiC particles. It can be observed that different degrees of crack termination and deflection occur near SiC particles. The reason for this phenomenon is that because Si and TiSi2 particles are brittle and easy to crack under shear stress, the strength of SiC particles is higher than that of Si and TiSi2 particles, and the propagation of cracks to SiC would not last, thus terminating or deflecting. Besides, there are differences in CTEs between SiC and TiSi2 or Si. When brazing is cooling, there would be different degrees of residual stress at grain boundaries, and thus induced crack deflection. When the shear force passes through the brazed joint, the crack termination and deflection will prolong the crack propagation path, which consumes additional energy and achieves the goal of improving the shear strength of the joint.

4. Conclusions

(1) It is feasible to braze SiC ceramic with CNT reinforced Si-24Ti composite brazing alloy. The interface of SiC joints is well-bonded by adding an appropriate amount of CNT, and a high strength joint is obtained.
(2) With the addition of CNT was 3 wt.%, the microstructure was refined in the braze zone. However, when it is further increased to 5 wt.%, too many SiC particles were formed in the braze zone, which makes it easy to produce holes in the brazing process.

(3) The maximum shear strength of Si-24Ti-3CNT brazed joint is 108 MPa, which is 21.3% higher than that of Si-24Ti-0CNT brazed joint (89MPa), while that of Si-24Ti-5CNT brazed joint is reduced to 55 MPa.

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