X. P. Xu, Q. M. Liu, C. Z. Xia* and J. S. Zou

Microstructure and Properties of Si_3N_4 Ceramics and 304 Stainless Steel Brazed Joint with Cu/Ag-Cu/Ti Laminated Filler Metal

<https://doi.org/10.1515/htmp-2016-0183>

Received August 22, 2016; accepted April 5, 2017

Abstract: Si_3N_4 ceramics and 304 stainless steel were joined by the Cu/Ag-Cu/Ti laminated filler metal. Interfacial microstructure of brazed joint and effect of brazing temperature and thickness of Cu foil on mechanical properties were studied in this paper. Research results showed that the interfacial microstructure of the brazed joint might be 304 stainless steel/ TiFe_2 /Ag-Cu eutectic + Cu(s,s)/Cu(s,s)/Cu(s,s) + Ag-Cu eutectic/ Cu_3Ti + TiN/ Si_3N_4 ceramics. With the increasing of the brazing temperature, four-point bending strength of the brazed joint initially increased, then decreased. The bending strength reached the maximum value of 53 MPa at 1153 K when the thickness of Cu foil was 500 μm . The bending strength reached the maximum value of 57 MPa with 1 mm thickness Cu interlayer under the brazing temperature of 1153 K.

Keywords: Si_3N_4 ceramics, laminated filler metal, interfacial microstructure, bending strength

Introduction

Engineering ceramics have many excellent physical and chemical properties, such as high hardness, high strength, high temperature resistance, corrosion resistance and abrasion resistance. These excellent properties make engineering ceramics widely used in the aerospace, optics, energy, machinery and other fields [1, 2, 3]. However, engineering ceramics have bad plasticity and toughness, which limit the application of engineering ceramics in these field [4]. Steel was well known for its high strength, good plasticity and toughness, so steel and

ceramics were joined in this paper in order to expand the application range of engineering ceramics [5, 6, 7].

Ceramics and steel are often joined by using brazing and diffusion bonding technologies. Ceramics and stainless steel have been joined by using the Ag-Cu eutectic filler metal with 4 μm thickness Ti foil coated on the surface of Si_3N_4 ceramics [8]. Si_3N_4 ceramics and 42CrMo steel have been joined by using Ag-Cu-Ti + Mo composite filler metal [9, 10]. J. Yang et al. successfully realized the joining of Si_3N_4 ceramics by adding TiN particles to the Ag-Cu-Ti filler metal [11]. X. G. Song et al. realized the joining of Si_3N_4 ceramics and TiAl intermetallics by introducing Si_3N_4 -particles into Ag-Cu-Ti filler metal [12]. These research results showed that the addition of active element Ti in the filler metals was helpful in improving the joining of ceramics and metals. Among these methods, the method of control the interlayer was most employed to release the stress and improve the performance of organization between ceramics and metals.

In this communication, the high residual stress existed in the brazing interface of ceramics and stainless steel [13], Cu foil was chosen as a buffer layer to release the stress between ceramics and 304 stainless steel. In addition, Z. D. Zou et al. found that the increase of Cu content would decrease the Ti activity in Ag-Cu-Ti filler metal [14]. In this paper, the traditional Ag-Cu based filler metal was replaced by Cu /Ag-Cu /Ti laminated filler metal to reduce the inhibition of Cu on the activity of Ti element.

Experimental

In this experiment, Si_3N_4 ceramics and 304 stainless steel were used as the base metal. Si_3N_4 ceramics were prepared by conventional Si_3N_4 ceramics, a lot of conductive TiC and other ingredients. It had excellent performance, such as high temperature creep, corrosion resistance, high temperature strength, wear resistance and good thermal shock resistance [15, 16, 17], and main performance parameters were shown in Table 1. In this paper, the size of both Si_3N_4 ceramics and 304 stainless steel was 19 mm $\times$ 19 mm $\times$ 8 mm. The Cu/Ag-Cu/Ti laminated

*Corresponding author: C. Z. Xia, Provincial Key Lab of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, China, E-mail: cz_xia@126.com

X. P. Xu: E-mail: xxpjust@126.com, Q. M. Liu:

E-mail: 405782283@qq.com, J. S. Zou: E-mail: zjzoujs@126.com, Provincial Key Lab of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, China

Table 1: Main properties of Si₃N₄ ceramics.

Density (g/cm ³)	Hardness (HRA)	Modulus of elasticity (GPa)	Coefficient of thermal expansion (10 ⁻⁶ /K)	Thermal conductivity coefficient [J/(cm·s·K)]	ΔH^0_{298} (KJ/mol)
3.25–3.35	92–94	304–330	3.2–3.5	0.155–0.293	–749

filler metal was composed of intermediate layer Cu foil, Ag-Cu eutectic filler metal and 5 μ m thickness Ti foil.

The surface of 304 stainless steel and Si₃N₄ ceramics was ground by sandpaper and grinding glass before being brazed, which ensured it had smooth surface but a little roughness. The oxide layer on the surface of Ag72Cu28 eutectic filler metal and Cu intermediate layer should be removed together before be used. After that, these base metal and filler metal were put in the acetone solution to remove surface grease and dirt for 15 min by ultrasonic cleaning machine. The arrangement of filler metal was shown in Figure 1. These specimens were put in KJL-2 type multi-function vacuum furnace. Firstly, the vacuum of furnace was pumped to 8.0×10^{-3} Pa. Secondly, the furnace chamber was heated with a rate of 10 K/min to 873 K and held at 873 K for 30 min. Thirdly, the furnace chamber was heated with a rate of 15 K/min to brazing temperature and held for 30 min. Finally, the specimens were cooled to room temperature with furnace.

The micro morphology of specimens and element distribution of the interface were observed and analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The phase constitution of brazed joint was studied by X-ray Diffraction (XRD). The four-point bending strength of specimens was tested in electronic universal testing machine. The moving speed of pressure head was 0.5 mm/min and the strength was measured by average value of five specimens.

Results and discussion

Microstructure structure of joint interface

Figure 2 was the joint interface of 304 stainless steel/Si₃N₄ ceramics which brazed at 1153 K and held for 30 min. Defects were not found in brazed interface and the layer of inter-phase was clear, which shown Cu/Ag-Cu/Ti laminated filler metal could connect ceramics and stainless steel well. The joint interface could be divided into three regions (II, III, IV) and two interfaces (I, V), as shown in Figure 2. In the interface of the brazed joint, the major elements in the joint regions were analyzed by EDS surface scanning technology. The results were

Figure 2: Interface of 304 stainless steel/Si₃N₄ ceramics joint. **Figure 1:** Arrangement sketch of filler metal.

shown in Figure 3. Interfaces I and V were mainly made of Ti element, but the distribution of Ti in the interface V was much brighter than that in the interface I. The brazed seam center was composed of rich Ag phase and rich Cu phase. The regions II and IV were formed by the interaction of Ag-Cu filler metal and interlayer Cu. Among them, the bright white pattern was the Ag-Cu eutectic structure.

Figure 4(a) shown the interface I was mutual staggered which formed by stainless steel, Ti and Ag-Cu filler metal together. The interface of ceramics, Ti foil and Ag-Cu filler metal was the key to complete the brazed joint. The interface V was flat and uniform, besides, the filler metal and ceramics formed a zonal reaction layer, as shown in Figure 4(b). The formation of this reaction layer may include infiltration, diffusion and reaction. The infiltration was the filler metal penetrated into the hole of ceramics surface after melting because of some holes were formed in the ceramics sintering process. The diffusion was elements diffused between filler metal and ceramics in the brazing process, besides, Ti was the main diffusion element. The reaction was the filler metal reacted with ceramics then formed the reaction layer. From Figure 5(d) and Table 2, it can be found that a large number of Si elements which from ceramics reacted with Ti elements on the ceramic side.

Different points were analyzed by EDS in order to determine the reaction of interfaces and regions. Table 2

(a)

(b)

Figure 4: Structure of brazing joint: (a) Microstructure near stainless steel side, (b) Microstructure near ceramics side.

Figure 3: The main elements distribution in the joint: (a) Distribution of Ti, (b) Distribution of Ag, (c) Distribution of Cu, (d) Distribution of Si.

Figure 5: EDS analysis of representative points: (a) point a, (b) point b, (c) point c, (d) point d.

was EDS analysis results of representative points which from point a to point f, and Figure 5 was the energy spectrum graph of points a, b, c and f.

The point a was mainly composed of Fe and Ti, and the mass percentage of Ti and Fe was 36 % and 64 %, respectively, as shown in Figure 5(a) and Table 2. TiFe_2 might be the preliminary phase according to Fe-Ti two-phase diagram. The formation of TiFe_2 phase was mainly the dissolution of Ti foil and the stainless steel reacted with Ti. According to Table 2, the content of Ag reached 90.75 % in the point d which proved it was rich Ag phase, besides, the content of Cu reached 99.29 % in the point c which proved it was rich Cu phase. According to the phase diagram of Cu-Ag, Ti-Ag, Cu-Ti and the results of EDS scan, it could be known that the white area was

Ag-based solid solution (Ag (s, s)) which contained a small amount of Cu and Ti. The middle layer of gray white area was Cu-based solid solution (Cu(s, s)) which contained a small amount of Ag. In the interface V, the point f was mainly composed of Ti and Si, which maybe Ti reacted with Si and formed Ti-Si compound, as shown in Figure 5(d). The reaction generated a variety of compounds due to the diffusion of Ti in ceramics, and a continuous and compact reaction layer was formed on the side of ceramics finally.

In order to further confirm the reaction products on the interface of ceramics, the fracture surface of ceramics side was analyzed by XRD. It can be seen from Figure 6 that the ceramics side of the reaction layer has $\text{TiN} + \text{Cu}_3\text{Ti}$. In conclusion, the interface structure of

Table 2: EDS analysis results of representative points in Figure 4.

Representative points	Elemental Composition (wt.%)						
	Si	Ti	Ag	Cu	Fe	Cr	Ni
a	0.37	29.57	1.17	6.03	51.42	7.23	4.21
b	0.18	0.60	70.72	28.91	0.19	—	—
c	0.24	—	0.26	99.29	0.06	0.14	—
d	0.38	1.09	90.75	7.53	—	0.25	—
e	—	0.31	67.15	32.04	0.21	0.09	0.20
f	31.75	59.54	3.49	4.42	0.51	0.24	0.05

Figure 6: The XRD of the fracture surface of Si₃N₄ ceramics side.

joint maybe 304 stainless steel/TiFe₂/Ag-Cu eutectic + Cu (s, s)/Cu (s, s)/Cu (s, s) + Ag-Cu eutectic/TiN + Cu₃Ti/Si₃N₄ ceramics.

Effects of brazing temperature on the mechanical properties

The mechanical properties of joint depended on the interface reaction directly. When the thickness of Cu foil was 500 μm and the brazing temperature was 1123 K, the interfacial reaction layer became clear on both sides of ceramics and stainless steel, especially on the side of ceramics. When brazing temperature reached to 1153 K, the high temperature made the reaction more turbulent and the atom diffusion became more and more apparent. With the thickening of TiN, the thickness of reaction layer on both sides of the base metal was increasing, and the reaction layer of ceramics side became more and more flat and density. The joint strength reached the maximum value of 53 MPa in this case. However, the brittle phase Ti-Si in reaction layer would continue to grow up when the brazing temperature reached 1193 K, so joint performance deteriorated under the action of brittle phases growing and thermal stress. The effect of brazing temperature on the strength of the joint was shown in Figure 7. In conclusion, 1153 K was the best brazing temperature when the thickness of Cu foil was 500 μm.

Effects of the thickness of Cu foil on mechanical properties

The residual stress of the brazed joint was easy to be released by the plastic deformation of Cu foil. With the increase of the thickness of Cu foil, the distribution of

Figure 7: The influence of brazing temperature on joint strength at room temperature.

joint stress and the mechanical properties of the joint could be improved obviously. The strength reached the maximum value of 57 MPa when brazing temperature was 1153 K and the thickness of Cu foil was 1 mm. The results of four points bending strength of the brazed joint was shown in Table 3.

Table 3: Four points bending strength of brazed joint.

Brazing temperature (T/K)	Thickness of Cu foil (μm)	Strength (MPa)
1153	350	42
1153	500	53
1153	1000	57

Conclusions

1. Cu/Ag-Cu/Ti laminate filler metal was used to braze the Si₃N₄ ceramics and 304 stainless steel. Fe₂Ti layer was formed on the stainless steel side and the middle layer was Cu (s, s) and Ag-Cu eutectic. TiN and Cu₃Ti were formed on ceramics side.
2. When the brazing temperature increased, the four-point bending strength of the brazed joint showed a significant upward trend. The strength reached the maximum value of 53 MPa at 1153 K when the thickness of Cu foil was 500 μm.
3. When the thickness of Cu foil increased, the strength of brazed joint showed a upward trend. The bending strength reached the maximum value of 57 MPa with 1 mm thickness Cu interlayer under the brazing temperature of 1153 K.

Funding: This project was supported by the National Natural Science Foundation of China (Grant No. 51405205) and the Project Funded by China Postdoctoral Science Foundation (2015M581751).

References

- [1] L.A. Plyasunkova, I.Y. Kelina and L.A. Chevykalova, *Refract. Ind. Ceram.*, 543 (2013) 6–8.
- [2] M.F. Wu, F. Liu, F.J. Wang and Y.X. Qiao, *Acta Metall. Sin.*, 51 (2015) 1129–1135.
- [3] Y.Q. Xing, J.X. Deng, X.T. Feng and S. Yu, *Mater. Design.*, 52 (2013) 22–27.
- [4] E.C. Hammel and O.I. Okoli, *Ceram. Int.*, 4010 (2014) 33–42.
- [5] C.Z. Xia, J. Yang, X.P. Xu and J.S. Zou, *High Temp. Mater. Process.*, 36 (2017) 477–483.
- [6] C.Z. Xia, Q.H. Liang, J.S. Zou and X.P. Xu, *High Temp. Mater. Process.*, 33 (2014) 293–298.
- [7] C.Y. Su, X.Z. Zhuang and C.T. Pan, *J. Mater. Eng. Perform.*, 233 (2014) 7–9.
- [8] R.M. Nascimento and A.E. Martinelli, *J. Mater. Sci.*, 4017 (2005) 8–10.
- [9] Y.M. He, J. Zhang and Y. Sun, *J. Eur. Ceram. Soc.*, 30 (2010) 3245–3251.
- [10] Y.M. He, J. Zhang and X. Wang, *J. Mater. Sci.*, 46 (2011) 2796–2804.
- [11] J. Yang and A.P. Wu, *T. China. Weld. I.*, 7 (2006) 18–20.
- [12] X.G. Song, J. Cao and Y.F. Wang, *Mater. Sci. Eng. A*, 528 (2011) 5135–5140.
- [13] H. Li, *Hot Work. Tech.*, 3 (2015) 13–17.
- [14] S.Y. Qu and Z.D. Zou, *T. China Weld. I.*, 4 (2003) 13–16.
- [15] Y.Q. Xing, J.X. Deng, Z. Wu and H.W. Cheng, *Appl. Surf. Sci.*, 265 (2013) 150.
- [16] H.G. Dong, Z.L. Yang and Z.R. Wang, *J. Mater. Eng. Perform.*, 2310 (2014) 230.
- [17] C. Xia, L. Wu and X. Xu, *Vacuum*, 136 (2017) 97–100.