Microstructure and properties of ZrO₂ ceramic and Ti-6A-4V alloy vacuum brazed by Ti-28Ni filler metal

Hong Li*, Xuan Liu¹, Haixin Huang¹

¹ College of Materials Science and Engineering, Beijing University of Technology, 100 Pingle Yuan, Chaoyang District, Beijing 100124, P. R. China
* Correspondence: hongli@bjut.edu.cn;
Received: 11.08.2019; Accepted: 30.09.2019

Abstract: Reliable ceramics/metal joints have an extensive application in the aerospace and biomedical area. However, ZrO₂ ceramic has not been investigated systematically compared to the Si₃N₄ and Al₂O₃ ceramic. Therefore, successful brazing of ZrO₂ ceramic and Ti-6A-4V alloy was achieved by using a binary active Ti-28Ni filler metal in this paper. The effect of holding time on the microstructure of ZrO₂ ceramic/filler metal interface and mechanical properties of brazed joints was investigated. The results indicated that the representative interfacial microstructure was ZrO₂ ceramic/Ti₅O/O₃O/Ti-rich phase/Ti₅Ni+/α-Ti. With the increase of holding time, the thickness of Ti-rich layer in the interface of ZrO₂/Ti-6Al-4V joint decreased obviously due to the diffusion of Ti atoms. Substantial brittle intermetallic compounds Ti₅Ni and Ni₄Ti₂O were formed in the joint, which were detrimental to the mechanical properties of the brazed joints. The maximum shear strength of joint was 112.7 MPa when brazed at 1060 °C for 10 min.

Key words: ZrO₂ ceramic; Ti-6A-4V alloy; vacuum brazing; interface microstructure; mechanical properties

Introduction

ZrO₂ ceramic is an important structural and functional ceramic material, which has excellent heat resistance, wear-resistance, corrosion resistance, and good biocompatibility [1,2]. Therefore, it is widely applied in biological medicine, metallurgy, aerospace, mechanical processing tool, e.g. [3÷5]. With the development of 5G technology, ZrO₂ ceramic back cover has become a new type of mobile phone body material due to its advantages in hardness, wear-resistance and signal transmittance performance. However, like many advanced ceramics, ZrO₂ ceramic is difficult to manufacture into complex shaped components due to its poor toughness and impact resistance. Therefore, its application has been limited to some extent. Ti-6Al-4V was successfully developed by the United States in 1850s and has been widely used in the aerospace industry since the 1950s due to its light weight, excellent biocompatibility, good tensile properties and corrosion resistance, which is complementary to ZrO₂ ceramic. Reliable joining of ZrO₂ ceramic to Ti-6Al-4V overcomes the above disadvantages.

To date, multiple methods including vacuum brazing, transient liquid phase diffusion bonding, and diffusion bonding have been used for ceramic-metal joining [6÷10]. Among these methods, vacuum brazing has become the main method to join ceramic and metal because of its unique advantages. Brazing of zirconia ceramic and Ti-6Al-4V has been extensively studied [11÷14]. The most of current research use active filler metal to join zirconia ceramic and Ti-6Al-4V alloy, such as Ag-Cu-Ti or Ti-Zr-Cu-Ni, which can directly braze zirconia ceramic and Ti-6Al-4V alloy without surface pre-metalizing of zirconia ceramic. In the brazing process, the active Ti diffuses into the ZrO₂Matrix when the filler metal melted, and react with O atoms on the ceramic surface to form TiOₓ (0<x<2) layer, which improves the wettability of ZrO₂ [15]. In addition, it prevents the further diffusion of O and Ti atoms into the ceramic, improving the wettability of the filler metal. Compared with other filler metal, Ti-based filler metal has obvious advantages when brazing Ti-6Al-4V alloy.

In this study the Ti-28Ni filler metal was used to braze ZrO₂ ceramic and Ti-6Al-4V alloy in this study. The effect of holding time on the microstructure and mechanical properties of the joint was investigated. The reaction products were analyzed by scanning electron microscopy (SEM) coupled with energy dispersive spectrometer (EDS), and X-ray diffraction (XRD).
Materials and experimental procedures

Yttria stability ZrO$_2$ ceramic (YSZ, 3mol%yttria) and Ti-6Al-4V were used in this study. Samples with the dimension of 10 nm × 5 nm × 5 mm and 30 nm × 10 nm × 10 mm were taken from the ZrO$_2$ ceramic and Ti-6Al-4V alloy respectively, using a diamond machine. A 50μm thick Ti-28Ni (wt.%) foil with the eutectic temperature of 942 °C was used as the filler metal. As shown in figure 1a, the XRD results show that the filler metal was mainly composed of TiNi and Ti phase.

Prior to brazing, the materials were ground by 400 grit, 800 grit and 1000 grit silicon carbide paper, and then ultrasonically cleaned for 15 min in acetone. The Ti-28Ni filler metal was placed between ZrO$_2$ ceramic and Ti-6Al-4V alloy samples to form a sandwich structure and a slight pressure was applied to ensure close contact between the filler metal and substrates by a graphite block as shown in figure 2a. The curve of brazing process was depicted in figure 1b, that the brazing temperature was 900÷1050 °C with the heating rate of 10 °C/min. The holding time was 10min at 900 °C and 5, 10, 15, 20 and 25 min respectively at 1050 °C. The joints were cooled down to room temperature in the furnace with the vacuum of (2.0÷5.0) ×10$^{-4}$ Pa.

The interface of ZrO$_2$/Ti-6Al-4V joints was characterized by scanning electron microscopy (SEM, HITACHIS-3400N) equipped with energy dispersive spectrometer (EDS). The shear strength of the joints was measured on a testing machine at a constant speed. The schematic of the shear test experiment was illustrated in figure 2b.

Results

Microstructure characteristics of ZrO$_2$ ceramic/filler metal interface

Because Ti-28Ni and Ti-6Al-4V alloys are both Ti-based alloys, the liquid Ti-28Ni filler metal could spread easily on the Ti-6Al-4V alloy and diffuse into the matrix metal, forming a strong bonding. Therefore, microstructure characteristics of the ZrO$_2$ ceramic/filler metal interface were analyzed in this study.

Figure 3 showed the microstructure and corresponding elements distribution of ZrO$_2$ ceramic/brazing seam interface at 1060 °C for 25 min. It can be seen that ZrO$_2$ ceramic/brazing seam interface was composed of three zones. Zone I and II were reaction layers near to ZrO$_2$ ceramic, and the thickness of zone I was only about 0.4 μm. Zone II was the diffusion-reaction layer. Ti and Ni atoms were distributed evenly in the whole interface, which played an important role in brazing of ZrO$_2$ ceramic/brazing seam interface, and further analysis was given below.
Figure 4 presented the magnified micrograph of the microstructure characteristic of the ZrO$_2$ ceramic/brazing seam interface, and the corresponding EDS results were shown in table I. The phase in the zone I (spot A in the Fig. 4a) was only composed of Ti and O elements with the atomic ratio of around 2:1, which was Ti$_2$O phase. The white phase (spot B in the Fig. 4a) was mainly composed of Ni, Ti and O elements with the atomic ratio close to 2:4:1, which corresponds to Ni$_2$Ti$_4$O phase. The energy spectrum of point C showed that the gray phase contained a large amount of Ti and a small amount of Al element, which conformed $\alpha$-Ti phase. The gray phase (D in the Fig. 4a) contained the higher content of element Ti (93.17 at%), but also contained a small amount of Ni, Al, V, which was the Ti-rich phase. The white strip phase (spot E in the Fig. 4b) mainly consisted of element Ti and Ni with their atomic ratio close to 2:1, which was the Ti$_2$Ni phase. And the white block phase (spot F in the Fig. 4b) was also the Ti$_2$Ni phase. Song X et al. [16] and Zhang et al. [17] also found the formation of Ni$_2$Ti$_4$O phase and Ti$_2$Ni phase during the study of joining of ZrO$_2$ ceramic and metal.

**Figure 4.** Microstructure of ZrO$_2$/filler metal interface at 1060 °C for 25 min

**Table I.** EDS chemical analysis (at. %) of different positions in figure 4

|     | Ti   | Ni  | O    | Al  | V    | Possible phase |
|-----|------|-----|------|-----|------|----------------|
| A   | 68.39| –   | 31.61| –   | –    | Ti$_2$O        |
| B   | 52.27| 35.74| 11.99| –   | –    | Ni$_2$Ti$_4$O  |
| C   | 94.03| –   | 5.97 | –   | –    | $\alpha$-Ti    |
| D   | 93.17| 4.12| –    | 1.20| 1.51 | Ti-Rich        |
| E   | 61.82| 36.53| –    | 1.65| –    | Ti$_2$Ni       |
| F   | 58.22| 40.18| –    | 1.60| –    | Ti$_2$Ni       |
| G   | 88.52| –   | 9.29 | 2.18| –    | $\alpha$-Ti    |
Ti₂O phase, Ni₂TiO phase and Ti₃Ni phase were also detected in the XRD patterns (fig. 6) obtained from the fracture surface of ZrO₂ side. Figure 7 showed the model of ZrO₂ ceramic/brazing interface reaction to layer formation mechanism according to the microstructure of ZrO₂ ceramic/brazing seam interface and the Ti-Ni binary phase diagram as shown in figure 5. It could be indicated that when the brazing temperature exceeded at 942 °C (melting point of Ti-28Ni), the filler metal between ZrO₂ and Ti-6Al-4V begun to melt and convert into the liquid. Active Ti in the liquid filler metal diffused into the ZrO₂ ceramic matrix under the diffusion driving force caused by the difference of concentration. Ti atoms accumulated on the surface of ZrO₂ ceramic and reacted with O to form Ti₂O reaction layer due to the strong affinity of element Ti and O. The overall reaction equation was as follows:

\[
\text{Ti} + \text{ZrO}_2 \rightarrow \text{Ti}_2\text{O} + \text{ZrO}_{2-x}
\]  

(1)

TiOₓ (0 < x < 2) was detected on the ZrO₂ ceramic side in many studies [13,18–20]. Durov et al. [21] and Hanson et al. [3] also found non-metered ZrO₂ (ZrO₂ₓ, 1 < x < 2) in the study and they proved that ZrO₂ ceramic lost oxygen atoms during brazing.

Fig. 5. Ti-Ni binary phase diagram

Fig. 6. XRD patterns obtained from the fracture surface of ZrO₂ side

From the above results, it could be seen that the formation of Ti₂O phase changed the state of the ceramic surface, and promoted the wettability of the liquid filler metal on the ceramic surface. Moreover, Ti₂O and Ni₂TiO phases had the characteristics of the metal, which played an important role in the brazing
The formation of Ti₂O and Ni₂TiO phases only consumed a small fraction of Ti and Ni atoms. With the decreasing brazing temperature, Ti and Ni atoms in the residual liquid phase were transformed into β-Ti firstly, and then turned into α-Ti and Ti₃Ni phase based on the eutectoid of β – Ti → α – Ti + Ti₂Ni according to the Ti-Ni binary phase diagram in figure 5. Therefore, the typical structure of ZrO₂ ceramic/brazing seam interface is ZrO₂ ceramic/Ti₂O/Ni₂TiO/Ti-rich phase/Ti₃Ni+α-Ti.

**Effect of holding time on microstructure evolution of ZrO₂ ceramic/filler metal interface**

Figure 7 displayed the microstructure evolution of ZrO₂ ceramic/filler metal interface at 1060 °C for different holding times. It could be seen that the holding time had a great influence on the interface structure of the joints, especially in Ti-rich layer as shown in figure 8. With the increasing holding time, the thickness of Ti-rich layer was gradually decreased. When the holding time was 5 min, the thickness of the Ti-rich layer is 19.2 μm due to the insufficient diffusion of Ti atoms. However, with the prolonging of the holding time, the thickness of the Ti-rich layer became narrowed. Its thickness was 5.2 μm when holding time was 20 min, and when the brazing time was 25 min the rich layer of Ti disappeared.

In addition, it could be seen that a continuous Ti₃Ni layer occurred near the Ti-rich layer, which based on the eutectic reaction of L → β – Ti + Ti₂Ni at 942°C. When the holding time was 5 min, Ti and Ni atoms did not have enough time to diffuse and react with each other to form the Ti₃Ni phase, so small amount of Ti₂Ni phases were formed. With the prolonging of the holding time, the amount of Ti₃Ni phases in the interface increased, which was detrimental to the mechanical properties of joints.

**Mechanical properties of brazed ZrO₂/Ti-6Al-4V joints**

The properties of the ZrO₂/Ti-6Al-4V joints brazed at different holding time were evaluated by shear test at room temperature. The results showed on figure 9 that the shear strength of ZrO₂/Ti-6Al-4V joints increased firstly and then decreased with the increasing holding time. The maximum average shear strength
of 112.7 MPa was obtained when brazing temperature was 1060 °C for 10 min. It could be seen that the thickness of Ti-rich layer had little influence on the joints. And the shear strength of joints only had 52.1 MPa when Ti-rich layer disappeared in the joints. With the increase of holding time, the amount of brittle intermetallic compounds TiNi gradually increased. The block TiNi phase appeared in the joints at 10 min, and the amount of the strip TiNi phases increased due to the insufficient time of diffusion and reaction between Ti and Ni atoms with the increasing holding time, which deteriorated the mechanical properties of the brazed joints. In addition, the thickness of TiO layer and TiNiO layer increased, which would produce a greater residual stress that deteriorated the joining properties.

![Fig. 9. Effect of holding time on the shear strength of ZrO2/Ti-6Al-4V joints at room temperature](image)

**Conclusions**

Vacuum brazing of ZrO2 ceramic and Ti-6Al-4V alloy was successfully achieved by using eutectic Ti-28Ni filler metal in this study. The main conclusions are summarized as follows:

1. The microstructure of ZrO2 ceramic/filler metal interface and the properties of joints were investigated in details. The interfacial microstructure of ZrO2 ceramic/brazing seam interface was ZrO2 ceramic/TiO/Ni:TiO/Ti-rich phase/TiNi+α-Ti.
2. The active Ti dissolved from filler metal and reacted with the ZrO2 ceramic to form the TiO layer, while the formation of TiO layer inhibited the diffusion of Ti into ZrO2 ceramic and then the further reaction of forming Ni:TiO layer adjacent to TiO layer. As the holding time increased, the diffusion of Ti and Ni atoms were accelerated and the formation of intermetallic compounds TiNi and Ni:TiO phase deteriorated the joining properties.
3. With the increase of holding time, the rising number of strip TiNi phase and the increasing thickness of TiO layer and TiNiO layer produce large residual stress, which reduce the mechanical properties of the joint. The maximum shear strength of joint was 112.7 MPa when brazed at 1060 °C for 10 min.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Feng J., Dai X., Wang D., Li R., Cao J., Microstructure evolution and mechanical properties of ZrO2/TiAl joints vacuum brazed by Ag–Cu filler metal, *Materials Science and Engineering: A*, 2015, Vol. 639, 739-746. [CrossRef]
2. Wang N., Wang D.P., Yang Z.W., Wang Y., Interfacial microstructure and mechanical properties of zirconia ceramic and niobium joints vacuum brazed with two Ag-based active filler metals, *Ceramics International*, 2016, Vol. 42(11), 12815-12824. [CrossRef]
3. Hanson W.B., Ironside K.L., Femie J.A., Active metal brazing of zirconia, *Acta Materialia*, 2000, Vol. 48(18-19), 4673-4676. [CrossRef]
4. Munoz M.C., Gallego S., Beltran J.I., Cerda J., Adhesion at metal-ZrO2 interfaces, *Surface Science Reports*, 2006, Vol. 61(7), 303-344. [CrossRef]
5. Dewidar M., Mohamed H.F., Lim J.K., A new approach for manufacturing a high porosity Ti-6Al-4V scaffolds for biomedical applications, *Journal of Materials Science and Technology*, 2008, Vol. 24(6), 931-935.
6. Jiang G.Q., Development of ceramic-to-metal package for BION microstimulator, 2005.
7. Dai X., Cao J., Liu J., Su S., Feng J., Effect of holding time on microstructure and mechanical properties of ZrO2/TiAl joints brazed by Ag-Cu filler metal, *Materials & Design*, 2015, Vol. 87, 53-59. [CrossRef]
[8] Smorygo J.S., Kim M.D., Kim T.G. Eom., Evolution of the interlayer microstructure and the fracture modes of the zirconia/Cu–Ag–Ti filler/Ti active brazing joints, Material Letters, 2007, Vol. 61(2), 613-616. [CrossRef]

[9] Guo W., Zhang H., Ma K., et al., Reactive brazing of silicon nitride to Invar alloy using Ni foam and AgCuTi intermediate layers, Ceramics International, 2019, Vol. 45(11), 13979-13987. [CrossRef]

[10] Sun R., Zhu Y., Guo W., et al., Microstructural evolution and thermal stress relaxation of Al2O3/1Cr18Ni9Ti brazed joints with nickel foam, Vacuum, 2018, Vol. 148, 18-26. [CrossRef]

[11] Liu Y.H., Hu J.D., Shen P., Han X.H., Li J.C., Microstructural and mechanical properties of jointed ZrO2/Ti–6Al–4V alloy using Ti–Zr–Cu–Ce amorphous brazing filler, Materials & Design, 2013, Vol. 47, 281-286. [CrossRef]

[12] Cao J., Song X.G., Li C., Zhao L.Y., Feng J.C., Brazing ZrO2 ceramic to Ti–6Al–4V alloy using NiCrSiB amorphous filler foil: Interfacial microstructure and joint properties, Materials Characterization, 2013, Vol. 81, 85-91.

[13] Dai X., Cao J., Liu J., et al., Interfacial reaction behavior and mechanical characterization of ZrO2/TC4 joint brazed by Ag-Cu filler metal, Materials Science & Engineering A, 2015, Vol. 646, 182-189. [CrossRef]

[14] Dai X., Cao J., Wang Z., et al., Brazing ZrO2 ceramic and TC4 alloy by novel WB reinforced Ag-Cu composite filler: Microstructure and properties, Ceramics International, 2017, Vol. 43, 15296-15305. [CrossRef]

[15] Bian H., Zhou Y., Song X., et al., Reactive wetting and interfacial characterization of ZrO2 by SnAgCu-Ti alloy, Ceramics International, 2019, Vol. 45(6), 6730-6737.

[16] Song X., Ben B., Hu S., et al., Vacuum brazing high Nb-containing TiAl alloy to Ti60 alloy using Ti-28Ni eutectic brazing alloy, Journal of Alloys & Compounds, 2017, Vol. 692, 485-491. [CrossRef]

[17] Zhang C., Qiao G., Jin Z., Interface Reaction Mechanism of Joining Alumina to Kovar with Ni-Ti Active Filler, Rare Metal Materials & Engineering, 2002, Vol. 31(5), 371-374.

[18] Liu Y., Hu J.D., Shen P., Guo Z.X., Liu H.J., Effects of fabrication parameters on interface of zirconia and Ti-6Al-4V joints using ZrC–Cu–Al–NiS amorphous filler, Journal of Materials Engineering and Performance, 2013, Vol. 22(9), 2602-2609. [CrossRef]

[19] Lin K.-L., Singh M., Asthana R., Characterization of yttria-stabilized-zirconia/stainless steel joint interfaces with gold-based interlayers for solid oxide fuel cell applications, Journal of the European Ceramic Society, 2014, Vol. 34(2), 355-372. [CrossRef]

[20] Durov A.V., Naidich Y.V., Kostyuk B.D., Investigation of interaction of metal melts and zirconia, Journal of Materials Science, 2005, Vol. 40(9-10), 2173-2178. [CrossRef]

© 2019 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).