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Article

Microstructure and properties of ZrO_2 ceramic and Ti-6A-4V alloy vacuum brazed by Ti-28Ni filler metal

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Abstract: Reliable ceramics/metal joints have an extensive application in the aerospace and biomedical area. However, ZrO_2 ceramic has not been investigated systematically compared to the Si_3N_4 and Al_2O_3 ceramic. Therefore, successful brazing of ZrO_2 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 ZrO_2 ceramic/filler metal interface and mechanical properties of brazed joints was investigated. The results indicated that the representative interfacial microstructure was ZrO_2 ceramic/Ti_2O/Ni_2Ti_4O/Ti-rich phase/Ti_2Ni+α-Ti. With the increase of holding time, the thickness of Ti-rich layer in the interface of ZrO_2/Ti-6Al-4V joint decreased obviously due to the diffusion of Ti atoms. Substantial brittle intermetallic compounds Ti_2Ni and Ni_2Ti_4O 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: ZrO_2 ceramic; Ti-6A-4V alloy; vacuum brazing; interface microstructure; mechanical properties

Introduction

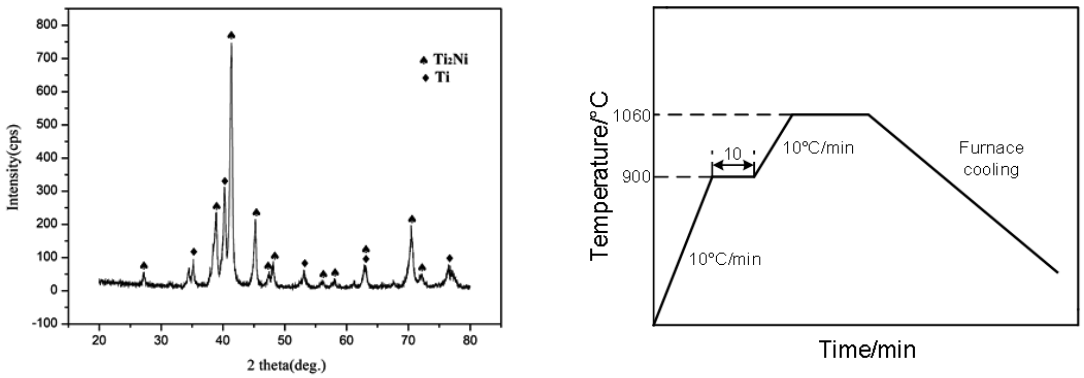
ZrO_2 ceramic is an important structural and functional ceramic material, which has excellent heat resistance, wear-resistance, corrosion resistance, and good biocompatibility [1,2]. Therefore, it is widely applied in biological medicine, metallurgy, aerospace, mechanical processing tool, e.g. [3÷5]. With the development of 5G technology, ZrO_2 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, ZrO_2 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 ZrO_2 ceramic. Reliable joining of ZrO_2 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 ZrO_2Matrix 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 ZrO_2 [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 ZrO_2 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

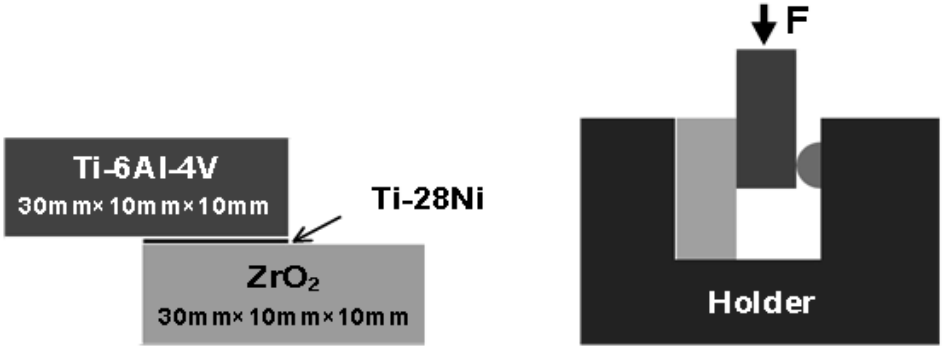
Yttria stability ZrO_2 ceramic (YSZ, 3mol%yttria) and Ti-6Al-4V were used in this study. Samples with the dimension of 10 nm × 5 nm × 5 mm and 30 nm × 10 nm × 10 mm were taken from the ZrO_2 ceramic and Ti-6Al-4V alloy respectively, using a diamond machine. A 50μm thick Ti-28Ni (wt.%) foil with the eutectic 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 Ti_2Ni and Ti phase.



(a) (b)

Fig. 1. a) XRD patterns of Ti-28Ni filler metal; b) curve of brazing cycle

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) $\times 10^{-4}$ 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.



(a) (b)

Fig. 2. Schematic diagram of: a) assembling brazing parts and b) shear test experiment

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.

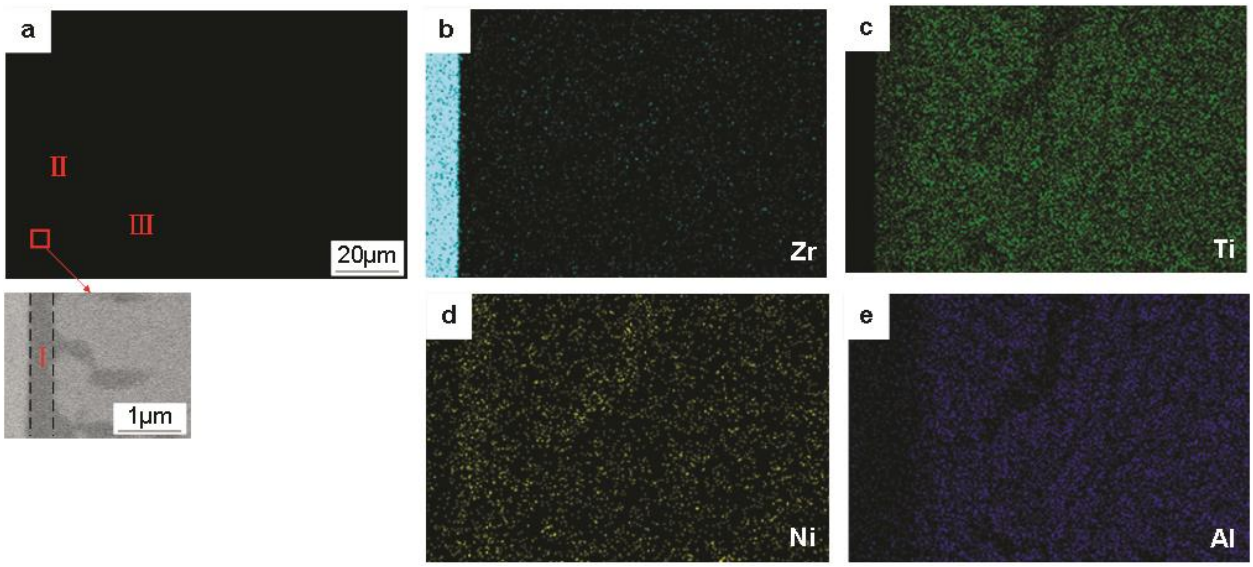


Fig. 3. a) Microstructure and (b÷f) corresponding element distribution images of Zr, Ti, Ni, O and Al of ZrO_2/filler metal interface at 1060 °C for 25 min

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_2O 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_2Ti_4O 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 α-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_2Ni phase. And the white block phase (spot F in the Fig. 4b) was also the Ti_2Ni phase. Song X et al. [16] and Zhang et al. [17] also found the formation of Ni_2Ti_4O phase and Ti_2Ni phase during the study of joining of ZrO_2 ceramic and metal.

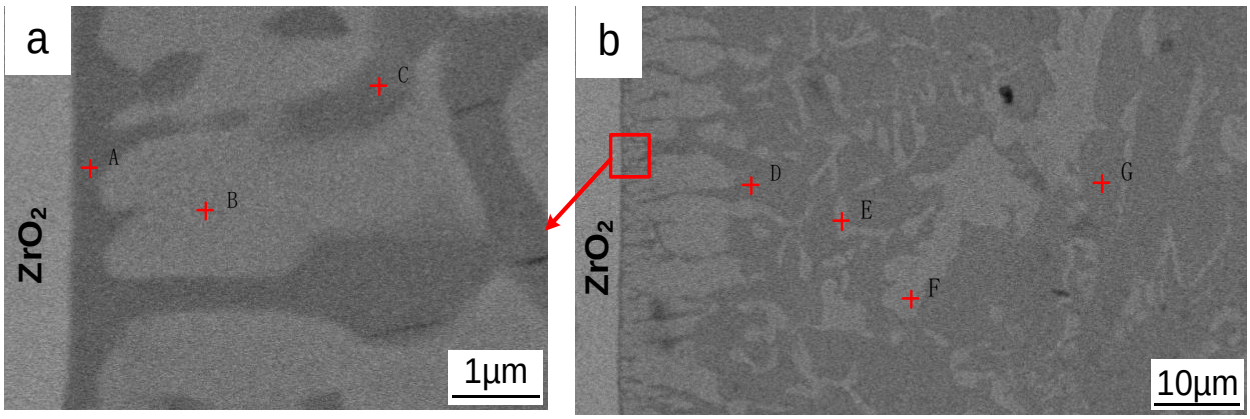


Fig. 4. Microstructure of ZrO_2/filler metal interface at 1060 °C for 25 min

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_2O
B	52.27	35.74	11.99	–	–	Ni_2Ti_4O
C	94.03	–	–	5.97	–	α-Ti
D	93.17	4.12	–	1.20	1.51	Ti-Rich
E	61.82	36.53	–	1.65	–	Ti_2Ni
F	58.22	40.18	–	1.60	–	Ti_2Ni
G	88.52	–	–	9.29	2.18	α-Ti

Ti_2O phase, Ni_2Ti_4O phase and Ti_2Ni phase were also detected in the XRD patterns (Fig. 6) obtained from the fracture surface of ZrO_2 side. Figure 7 showed the model of ZrO_2 ceramic/brazing interface reaction to layer formation mechanism according to the microstructure of ZrO_2 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 ZrO_2 and Ti-6Al-4V begun to melt and convert into the liquid. Active Ti in the liquid filler metal diffused into the ZrO_2 ceramic matrix under the diffusion driving force caused by the difference of concentration. Ti atoms accumulated on the surface of ZrO_2 ceramic and reacted with O to form Ti_2O reaction layer due to the strong affinity of element Ti and O. The overall reaction equation was as follows:

$$Ti + ZrO_2 \rightarrow Ti_2O + ZrO_{2-x} \quad (1)$$

TiO_x ($0 < x < 2$) was detected on the ZrO_2 ceramic side in many studies [13,18÷20]. Durov et al. [21] and Hanson et al. [3] also found non-metered ZrO_2 (ZrO_{2-x}, $1 < x < 2$) in the study and they proved that ZrO_2 ceramic lost oxygen atoms during brazing.

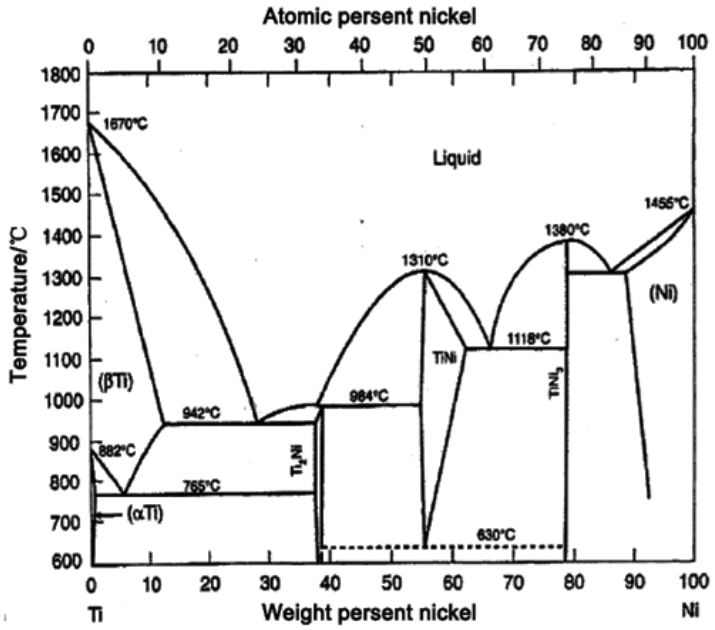


Fig. 5. Ti-Ni binary phase diagram

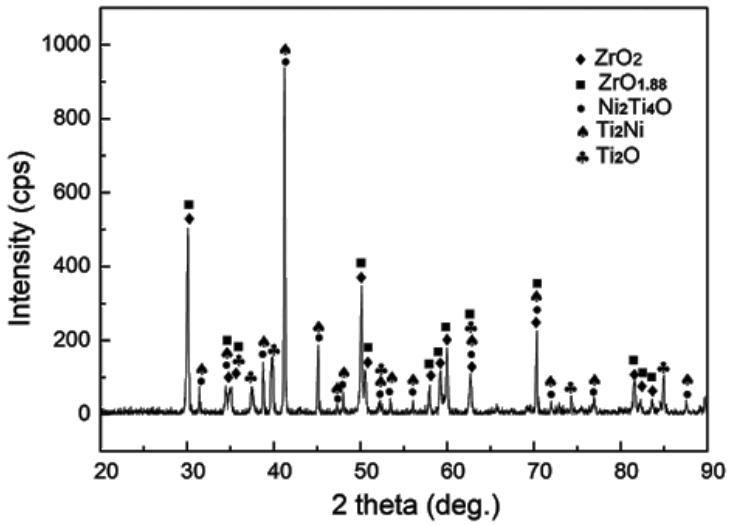


Fig. 6. XRD patterns obtained from the fracture surface of ZrO_2 side

From the above results, it could be seen that the formation of Ti_2O phase changed the state of the ceramic surface, and promoted the wettability of the liquid filler metal on the ceramic surface. Moreover, Ti_2O and Ni_2Ti_4O phases had the characteristics of the metal, which played an important role in the brazing

process. The formation of Ti_2O and Ni_2Ti_4O 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 Ti_2Ni phase based on the eutectoid of $\beta - Ti \rightarrow \alpha - Ti + Ti_2Ni$ according to the Ti-Ni binary phase diagram in figure 5. Therefore, the typical structure of ZrO_2 ceramic/brazing seam interface is ZrO_2 ceramic/Ti_2O/Ni_2Ti_4O/Ti-rich phase/Ti_2Ni+α-Ti.

Effect of holding time on microstructure evolution of ZrO_2 ceramic/filler metal interface

Figure 7 displayed the microstructure evolution of ZrO_2 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.

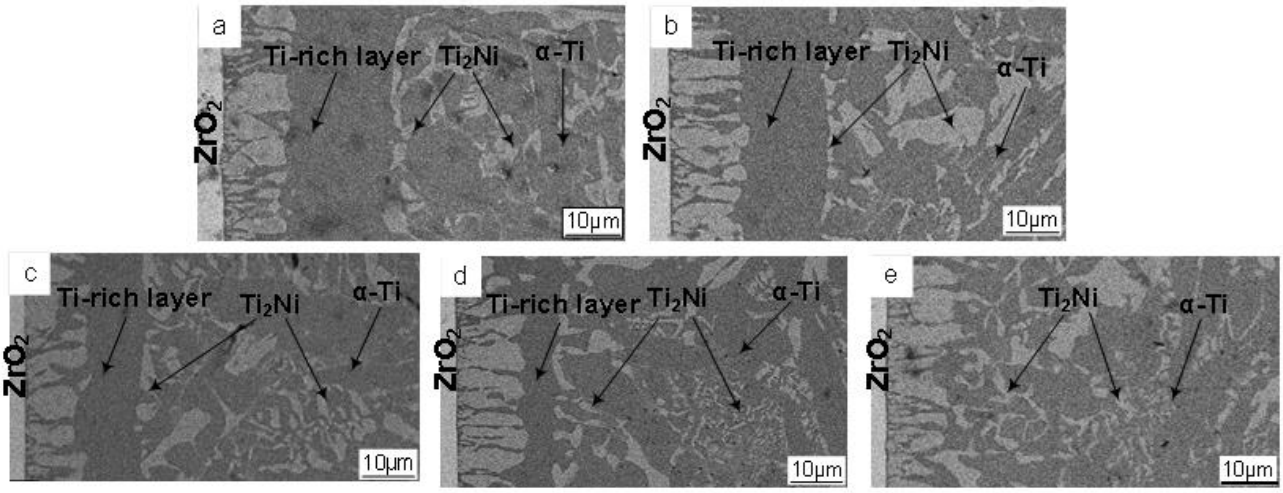


Fig. 7. Microstructure of ZrO_2/Ti-28Ni interface at 1060 °C for: a) 5 min; b) 10 min; c) 15 min; d) 20 min and e) 25 min

In addition, it could be seen that a continuous Ti_2Ni layer occurred near the Ti-rich layer, which based on the eutectic reaction of $L \rightarrow \beta - Ti + Ti_2Ni$ at 942°C. When the holding time was 5min, Ti and Ni atoms did not have enough time to diffuse and react with each other to form the Ti_2Ni phase, so small amount of Ti_2Ni phases were formed. With the prolonging of the holding time, the amount of Ti_2Ni phases in the interface increased, which was detrimental to the mechanical properties of joints.

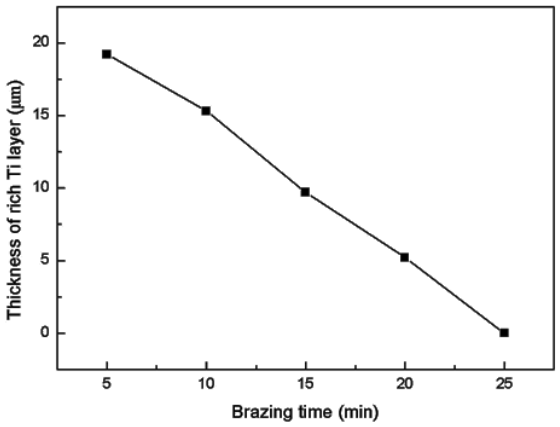


Fig. 8. Variation of thickness of Ti-rich layer with brazing time

Mechanical properties of brazed ZrO_2/Ti-6Al-4V joints

The properties of the ZrO_2/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 ZrO_2/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 Ti_2Ni gradually increased. The block Ti_2Ni phase appeared in the joints at 10 min, and the amount of the strip Ti_2Ni 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 Ti_2O layer and Ti_2Ni_4O layer increased, which would produce a greater residual stress that deteriorated the joining properties.

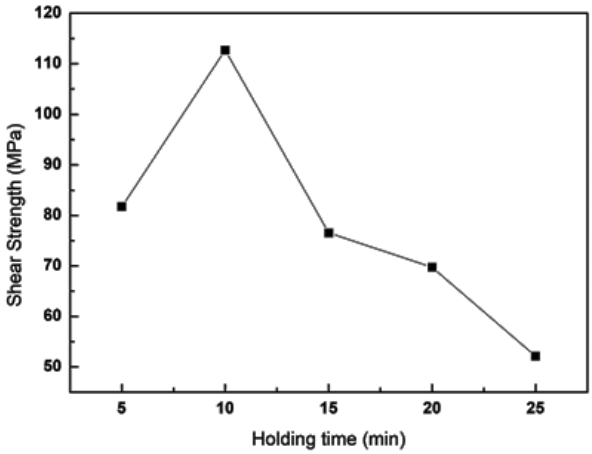


Fig. 9. Effect of holding time on the shear strength of ZrO_2/Ti-6Al-4V joints at room temperature

Conclusions

Vacuum brazing of ZrO_2 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 ZrO_2 ceramic/filler metal interface and the properties of joints were investigated in details. The interfacial microstructure of ZrO_2 ceramic/brazing seam interface was ZrO_2 ceramic/Ti_2O/Ni_2Ti_4O/Ti-rich phase/ Ti_2Ni+α-Ti.
2. The active Ti dissolved from filler metal and reacted with the ZrO_2 ceramic to form the Ti_2O layer, while the formation of Ti_2O layer inhibited the diffusion of Ti into ZrO_2 ceramic and then the further reaction of forming Ni_2Ti_4O layer adjacent to Ti_2O layer. As the holding time increased, the diffusion of Ti and Ni atoms were accelerated and the formation of intermetallic compounds Ti_2Ni and Ni_2Ti_4O phase deteriorated the joining properties.
3. With the increase of holding time, the rising number of strip Ti_2Ni phase and the increasing thickness of Ti_2O layer and Ti_2Ni_4O 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.

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