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Abstract
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Interfacial microstructure and shear strength of TC4 alloy joints vacuum brazed with Ti-Zr-Ni-Cu filler metal

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ABSTRACT

Ti–6Al–4V alloy was successfully vacuum brazed with a commercial Ti-37.5Zr-10Ni-15Cu (wt.%) filler metal. The effect of brazing temperature and time on the microstructure and shear strength of the brazed joints were investigated. When the brazing temperature was 905 °C for 10 min, the typical interfacial microstructure of the brazed joint were a single layer of α-Ti with a high concentration of Ti, α-Ti, (Ti, Zr)2(Cu, Ni) intermetallic compound and eutectoid microstructure. Increasing the brazing temperature and time are beneficial to eliminate the (Ti, Zr)2(Cu, Ni) intermetallic compound that degrades the properties in the brazed joint. The shear strength of the brazed joint increases first and then decreases with brazing temperature,
and increases with the extended holding time. The maximum shear strength of the brazed joint is 635.77 MPa at a brazing temperature of 920 °C for 30 min due to the high content of columnar α-Ti. Extending the brazing time is obviously beneficial to increasing the strength. The microstructure and shear strength of the brazed joint are highly dependent on brazing temperature and time.

Keywords: Titanium alloy  Vacuum brazing  Microstructure  Shear strength

1. Introduction

TC4 (Ti-6Al-4V) is a common titanium alloy that plays an important role in the industry, which is a typical duplex alloy including α phase (hexagonal close packed, hcp) and β phase (body-centered-cubic, bcc) [1]. Due to its excellent corrosion resistance, small density, high specific strength and good plasticity, TC4 has been widely used in aerospace, nuclear, shipbuilding, biomedical and other industries [2-4]. The importance of TC4 is also reflected in its huge application volume, and specifically; has captured 60% of the market share of all commercial titanium alloys for more than 60 years [5]. However, its connection remains a problem, being an important part of the processing and application.

Many joining methods, such as fusion welding, diffusion bonding, and brazing are used for the joining of titanium alloys [6, 7]. The effect of fusion welding on the properties of the base metal is more obvious because it has a large heat affected zone and the titanium alloy is susceptible to contamination. Diffusion bonding requires rigorous surface treatment, long connection time and high temperature and pressure to be applied [8]. Brazing has become an important method of joining titanium alloys in
complex and demanding structural applications [6]. However, titanium alloy is easy to absorb nitrogen, oxygen and other gases at high temperatures and chemically react to form nitrides and oxides, because the chemical properties of it become more and more active with temperature [4, 9, 10]. This will seriously deteriorate the joining quality.

Vacuum brazing has the advantages of being free from impurity gas contamination, small deformation of the welding specimen, less influence on the mechanical properties of the base metal [5], connection of complicated structures [8], and simultaneous welding of a large number of workpieces. So, vacuum brazing is also considered as an ideal industrial process to connect titanium alloy [6].

The strategy of selecting suitable filler metal fundamentally affects brazing performance. Ti–Cu–Ni and Ti–Zr–Cu–Ni brazing alloys are ideal for brazing titanium alloys because they have good wettability with the parent metal and tend to form a brazed joint that is firmly bonded and corrosion resistant [11-13]. Both the filler alloys contain Cu and Ni, which are added as melting point depressants (MPDS) [14, 15]. The brazing temperature of Zr-containing Ti–Zr–Cu–Ni filler metal relatively lower[15, 16], because its melting temperature is about 100 °C lower than that of Ti–Cu–Ni filler alloy [5]. And the addition of Zr can increase the wettability of Ti-based filler metal to base metal, which is beneficial to obtain sound brazed joint [17].

The brazing technique including brazing temperature and time plays a crucial role in the brazing process of the titanium alloy. The brazing temperature depends on the melting temperature of the filler metal to a certain extent, while the brazing time should change obviously with the brazing temperature. When the brazing temperature
exceeds β phase transition temperature of TC4 at 990 °C, the microstructure of the substrate transforms into acicular (α + β)-Ti and becomes larger and coarser, which leads to deterioration of the properties of the base material [15, 18]. For the brazing, the adequate technique will be paramount to controlling weld structure in order to inhibit the presence of intermetallic compounds or to reduce their quantity in the brazed joint. It can also reduce the deterioration of the substrate properties due to coarse grain and inhibit the corrosion of substrate caused by molten filler metal.

C.T. Chang et al. investigated the Ti-Cu-Ni filler alloy brazing Ti–6Al–4V and Ti-15-3, and reported that the Cu and Ni enrichment is unfavorable to the performance of the brazed joint, which can be reduced or even eliminated by increasing brazing temperature and holding time [19]. Similarly, R.K. Shiue et al. used Ti-Cu-Ni metal filler to braze Ti3Al and TC4 [20]. They all found that the shear strength of the brazed joint increases with the brazing temperature. E. Ganjeh brazed TC4 in an argon atmosphere using Ti-based and Zr-based amorphous brazing filler metal. He pointed out that the bulk (Ti, Zr)2(Cu, Ni) intermetallic compound are formed during the brazing process, which are the main reason for the deterioration of brazed joint performance [5]. S.J. Pang et al. reported the vacuum brazing of TC4 with a multi-component TiZr-based amorphous brazing filler metal with a low content of Cu and Ni. The melting point of the brazing alloy is about 910 °C, and the shear strength of brazed joint can reach 413 MPa [15]. Y.C. Du et al. used two kinds of Ag-based brazing materials to braze TC4. The brazing temperature is low, and the shear strength of brazed joint is up to 153 MPa [21]. However, Ag-based brazing
fillers are expensive and difficult to be widely used. A lower brazing temperature coupled with technique is an ideal choice for TC4 connection.

In order to obtain better TC4 connection performance at lower temperatures, and referring to the previous beneficial brazing studies, vacuum brazing TC4 was conducted using a conventional commercial Ti-Zr based brazing filler metal Ti-37.5Zr-10Ni-15Cu (wt.%). In this work, the effect of brazing temperature and time on the microstructure evolution and shear strength of the brazed joints were studied. Furthermore, the fracture locations and fracture morphology of the brazed joints were also investigated.

2. Materials and experimental procedures

The substrate used in this experiment is TC4, its main chemical composition is listed in Table 1. The samples for micromorphology analysis (20 × 4 × 2 mm$^3$ and 10 × 4 × 2 mm$^3$) and shear strength test (10 × 4 × 4 mm$^3$ and 8 × 4 × 4 mm$^3$) were prepared by wire cutting, and the brazing samples were mounted as shown in the Fig. 1. It can be seen that the sample for microstructure analysis is a docking assembly model, and the samples for shear strength test is a lap assembly model, which are also the two basic forms of the brazed joint and are depicted by Fig. 1(a) and (b), respectively. It is necessary to clean the substrate before brazing. The substrate joint surface was polished with 100# SiC paper, and then ultrasonically cleaned in anhydrous ethanol for 300 seconds and dried in air.
Fig. 1. Schematic diagram of assembly of brazed specimens: (a) microstructure analysis; (b) shear strength test.

### Table 1

Main chemical composition of TC4.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>C</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(wt.%)</td>
<td>Bal.</td>
<td>6.0</td>
<td>4.0</td>
<td>≤0.30</td>
<td>≤0.08</td>
<td>≤0.05</td>
<td>≤0.20</td>
</tr>
</tbody>
</table>

A common commercial brazing powder Ti-37.5Zr-10Ni-15Cu (wt.%) with an average particle size of 35 μm was used. The brazing powder was added with trichloroethylene to form a paste, which facilitates the assembly of the brazed samples and improves their stability. The prepared paste brazing alloy was paint in the middle of two TC4 substrates like a sandwich, and the thickness of the paste was controlled at about 50 μm. A 15N graphite plate was placed on the workpiece to ensure close contact between the filler metal and the substrate during brazing. The assembled samples were carefully placed in a vacuum brazing furnace, and the vacuum atmosphere was preset to better than 3 × 10⁻³ Pa. In order to determine the brazing temperature, the melting characteristics of the brazing alloy was measured by differential scanning calorimetry (DSC) at a heating rate of 20 °C/min. The Fig. 2(a) shows the DSC curve of the filler metal. Its initial melting temperature $T_m$ is 831 °C and the melting temperature $T_f$ is 867 °C [22, 23]. Meanwhile, the filler metal is a
eutectic composition, and its melting range \( (T_l-T_m) \) is narrower to 36 °C, which has good fluidity \([15]\). Therefore, the brazing temperature is selected from 890~950 °C, which is 23~83 °C higher than the \( T_l \) of the filler metal, but lower than the \( \beta \) phase transition temperature of the TC4 substrate. The holding time was chosen to be 5~30 min in order to avoid corrosion of the substrate due to the filler metal. The time-temperature profile during the vacuum brazing cycle is shown in the Fig. 2(b). Prior to the temperature reaching the final brazing temperature, the holding process is primarily to minimize potential temperature gradients in brazing.

![Fig.2.](image)

**Fig.2.** (a) DSC curve of the filler metal and (b) time-temperature profile of the brazing cycle.

The brazed joint samples were sanded and polished after being cut by wire cutting perpendicular to the cross-sectional direction. \( \text{Al}_2\text{O}_3 \) was used as a polishing paste. The cross section of the samples was observed by a scanning electron microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS), and the distribution of elements were detected by EDS. The shear strength at room temperature was measured on a UTM 2203 universal mechanical testing machine.

The brazed specimens were loaded at a constant speed of 0.5 mm/min. In order to
exclude the random factors of the experiment, at least three brazing samples were taken for shearing test in each brazing condition [6]. The fracture location and fracture morphology were observed by SEM and the fracture surface reaction products were investigated by Ultima IV X-ray diffraction (XRD) after shear testing. Cu Kα was selected as the source of X-rays with a scan range of 30 to 90 ° and a speed of 8 °/min.

3. Results

3.1. Typical interfacial microstructure of the brazed joint

Figure 3(a) shows the typical interfacial microstructure of the TC4 brazed joint at a brazing temperature of 905 °C for 10 min. It can be clearly seen that the brazed joint is tightly connected without obvious defects such as pores and cracks. A dense but irregular area is formed in the brazed joint, mainly including the zone I adjacent to the substrate, the discontinuous zone II, the lamellar zone III and the central zone IV, which reflects the good physical and chemical metallurgical bonding of the filler metal to the substrate.

In order to clarify the microstructure of the brazed joint, the main structural zones were selected for chemical composition analysis. The chemical composition of each point in Fig. 3(a) was analyzed and is listed in Table 2. According to the results in Table 2 and in combination with the morphology of the microstructure in Fig. 3(a), a large amount of gray phase is contained in the zone I, which is an α-Ti layer. A reasonable assumption about its formation is that the Ti atoms in the substrate are continuously dissolved and diffused, and eventually aggregate due to the inhibition of
the zone II. The Ti contents of point A1 and A2 reach 98.14 and 97.64, respectively. This indicates that the large amount of gray phase contained in the zone I adjacent to the substrate has very high Ti concentration, although there is a Ti concentration gradient across the brazed joint caused by diffusion. A fine white strip phase penetrates into the zone I through the discontinuous zone II. It can be speculated from the map distribution of the elements in Fig. 4 that the fine strip phase mainly contains Zr, Cu and Ni, and that its structure is inferred to be (Ti, Zr)\(_2\)(Cu, Ni). Its formation may be due to the residual filler metal infiltrating into the grain boundary of single α-Ti layer with lower hardness, which is considered as intergranular penetration [24]. Generally, the higher the concentration of Ti in the Ti-based alloy, the higher the plasticity and the lower the corresponding hardness. Point B in the zone II still contains mainly Ti and a small amount of Al. The structure of the zone II is reasonably confirmed α-Ti, due to that Al is a common stabilizer for α-Ti [5, 8, 25]. According to the composition feature and tissue morphology, the zone III and IV where C and D are located is typical eutectoid microstructure, comprising dark gray flake of α-Ti and bright white flake of (Ti, Zr)\(_2\)(Cu, Ni) [6, 26, 27]. The white phase E mainly contains Ti, Zr, Cu and Ni, and the stoichiometry of Ti + Zr and Cu + Ni is approximately to 2:1, which is accordingly identified as a typical bulk (Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound [8, 16, 26]. Due to the higher concentration of Cu and Ni in the central zone IV, the bulk (Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound accumulates and forms a network, in the mesh of which the eutectoid microstructure is distributed. During brazing, a large amount of Ti continuously diffuses from the substrate to the
molten solder, and the diffusion decreases with the increase of distance. But meanwhile Cu and Ni in the center part of the filler metal are relatively difficult to dissolve and diffuse and less diluted by diffusion of Ti from the substrate. Thus, the enrichment of Cu and Ni in the central part of the weld section is formed, although the overall content is lower than their initial content in the filler metal.

**Fig.3.** (a) and (b) are the microstructures of the brazed joints at temperatures of 905 and 890 °C for 10 min, respectively, and (c) is the distribution of elements along the direction of the arrow in (b).
Table 2

EDS chemical composition (at.%) analysis results and possible phases in Fig. 3(a).

<table>
<thead>
<tr>
<th>Zone</th>
<th>Position</th>
<th>Ti</th>
<th>Zr</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Al</th>
<th>Possible phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A1</td>
<td>98.14</td>
<td>0.14</td>
<td>0.20</td>
<td>0.19</td>
<td>0.66</td>
<td>0.67</td>
<td>α-Ti (high Ti concentration)</td>
</tr>
<tr>
<td>I</td>
<td>A2</td>
<td>97.64</td>
<td>0.25</td>
<td>0.45</td>
<td>0.23</td>
<td>0.57</td>
<td>0.86</td>
<td>α-Ti (high Ti concentration)</td>
</tr>
<tr>
<td>II</td>
<td>B</td>
<td>82.25</td>
<td>7.39</td>
<td>3.57</td>
<td>3.38</td>
<td>0.78</td>
<td>2.63</td>
<td>α-Ti</td>
</tr>
<tr>
<td>III</td>
<td>C</td>
<td>81.23</td>
<td>7.56</td>
<td>4.18</td>
<td>3.09</td>
<td>1.75</td>
<td>2.18</td>
<td>eutectoid microstructure</td>
</tr>
<tr>
<td>IV</td>
<td>D</td>
<td>51.45</td>
<td>20.07</td>
<td>13.83</td>
<td>8.74</td>
<td>0.93</td>
<td>4.98</td>
<td>eutectoid microstructure</td>
</tr>
<tr>
<td>IV</td>
<td>E</td>
<td>41.10</td>
<td>24.26</td>
<td>16.44</td>
<td>12.45</td>
<td>0.80</td>
<td>4.94</td>
<td>(Ti, Zr)(_2)(Cu, Ni)</td>
</tr>
</tbody>
</table>

The interfacial microstructure of the brazed joint at a brazing temperature of 890 °C for 10 min in Fig. 3(b) is similar to that in Fig. 3(a). Fig. 3(c) shows the distribution of the elements in the direction of the corresponding arrow in Fig. 3(b). It can be seen that the chemical composition of the bulk (Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound is very close to the original filler metal, which also directly confirms that its essential source is the filler metal. Fig. 4 is a map of the EDS composition of the brazed joint. Due to the interaction between the filler metal and the substrate, there are Al and V in the brazing seam, and Zr, Ni and Cu are also present in the substrate near the brazing seam. In addition, according to the dissolved mixed enthalpy, the binding ability of Zr to Cu and Ni is stronger than that of Ti, so Zr is consistent with the distribution regions of Cu and Ni[28]. The results of elemental distribution maps in Fig. 4 are consistent with those of line scanning in Fig. 3(c).
Fig. 4. (a) The typical interfacial microstructure of the brazed joint at 890 °C for 10 min, and the corresponding element distribution map (b) Ti; (c) Al; (d) V; (e) Zr; (f) Cu and (g) Ni.

3.2. Shear strength of the brazed joint

The strength of the brazed joint has a critical impact on its application. Fig. 5(a) shows the room temperature shear strength of the brazed joint at different brazing temperatures with a time of 10 min. It can be seen that the minimum shear strength of the brazed joint is 271.57 MPa at the brazing temperature is 890 °C, whereas the maximum shear strength is obtained at 920 °C. The shear strength of the brazed joint
increases first and then decreases with brazing temperature. Fig. 5(b) gives the room temperature shear strength of the brazed joint, which was brazed at 920 °C for different time. The maximum shear strength of the brazed joint is 635.77 MPa at a brazing temperature of 920 °C for 30 min, as shown in detail in Fig. 5(c). The shear strength of the brazed joint increases with time. Extending the brazing time is obviously beneficial to strengthening the brazed joint.

Fig.5. (a) Shear strength of brazed joints with different brazing temperatures for 10 min, (b) shear strength of brazed joints with different brazing time at 920 °C and (c) shear stress-strain curves of the brazed joints at 920 °C for 30 min.

4. Discussion

4.1. Transformation of phase structure in the brazed joint

The formation of brazed joint is the result of mutually diffusive transport and dissolve between the elements of the filler metal and the substrate, and the main phase
transitions are discussed. When the brazing temperature was lower than the $T_m$ of the filler metal, only the solid diffusion of the substrate and the filler metal occurred. Once the temperature reached the $T_m$ of the filler metal, the filler metal began to melt with infiltrating into the substrate [23, 29]. The concentration gradient between the elements of the filler metal and the substrate drives the mutual diffusion [12, 22]. The Ti, Al, and V in the TC4 base metal diffused toward the molten filler metal, and Cu, Ni and Zr in the molten filler metal diffused into the interface region between the substrate and the molten filler metal, the diffusion result of which is manifested by the microstructure morphology in Fig. 3(a) and (b), and the elemental line distribution in Fig.3 (c). The diffusion of the element was conducive to the formation of the brazed joint. However, the diffusion has obvious orientation in the formation process of brazed joint. The thickness ($\sim 100$ $\mu$m) of the brazing seam is approximately twice the initial thickness ($\sim 50$ $\mu$m) of the filler metal, as shown in Fig. 3(a) and (b). This is because the atoms, especially Ti and Al in the present TC4 base metal, diffuse to the molten state more strongly, resulting in the occurrence of more atoms diffusion from the substrate into the molten filler metal [16]. And the role of filler metal infiltrating into the substrate can not be ignored [23, 29]. The higher concentration of Ti in the liquid pool provided favorable conditions for the formation of $\beta$-Ti, so that the transformation of $L \rightarrow L+\beta$-Ti occurred [24, 26]. Meanwhile, the diffusion at a certain temperature could be blocked with time. The concentration of Zr, Cu and Ni in the liquid pool were reduced, while the concentration of Ti and Al were increased, as shown in Fig.3 (c). This caused the melting point of the residual filler metal to rise, so
that it suffered isothermal solidification, impeding the diffusion.

Ti and Cu can be considered as Zr and Ni in some cases, and the phase composed of these four elements can be considered as \((\text{Ti, Zr})_2(\text{Cu, Ni})\) [16, 18, 22-24]. In the cooling step, when the temperature is lower than the \(\beta-\alpha\) phase transition temperature, \(\alpha\)-Ti is generated from \(\beta\)-Ti, which mainly corresponds to the zone I and II in Fig. 3(a). The change in the residual filler metal concentration is due to the formation of \(\beta\)-Ti and results in the formation of a bulk \((\text{Ti, Zr})_2(\text{Cu, Ni})\) intermetallic compound, as shown by phase E in Fig. 3(a). Cu and Ni were contained in \(\beta\)-Ti due to the interaction of the filler metal and the substrate. According to the Ti-Cu and Ti-Ni phase diagrams, the solid solubility of Cu and Ni in \(\beta\)-Ti is larger than that in \(\alpha\)-Ti [6, 8, 12, 15, 29]. The eutectoid reaction \(\beta\)-Ti\(\rightarrow\alpha\)-Ti\(+\)(Ti, Zr)\(_2\)(Cu, Ni) then occurred, which corresponds to the formation of the eutectoid microstructures C and D as shown in Fig. 3(a). Therefore, \(\beta\)-Ti is absent in the brazed joint at room temperature due to it completely decomposed into \(\alpha\)-Ti and \((\text{Ti, Zr})_2(\text{Cu, Ni})\) during cooling with the furnace.

4.2. Effect of brazing temperature and time on microstructure of the brazed joint

Figure 6(a), (b), (c), (d) and (e) display the microstructures of the brazed joints at temperatures of 890, 905, 920, 935 and 950 °C for 10 min, respectively. It can be seen that the microstructure of the brazed joints has occurred significant changes as the brazing temperature increases, which means that the brazing temperature plays a crucial role in the brazing cycle. It is noted that the thickness of the brazing seam is not significantly increased by about 105 μm. With the increasing of brazing temperature, the dissolution and diffusion of the substrate to the filler metal are
enhanced, whereas more filler metal flows to the substrate at the same time due to similar effects, and these two opposite roles are very close. This also reflects the wettability of the filler metal. The thickness of the zone I is slightly increased due to an increase in diffusion of Ti, and the maximum thickness is approximately to 36 μm. However, the white strip phase (Ti, Zr)_{2}(Cu, Ni) permeating the zone I is reduced because of the reduction of residual filler metal. Moreover, zone III becomes irregular and messy, which also reflects a more intense reaction in the brazing seam, as shown in Fig. 6(e). This is attribute to the higher diffusion coefficient of the element [16, 23]. The pictures inserted in Fig. 6(a) and (c) are a magnification of the eutectoid microstructure in the wireframe, respectively. It can be seen that the eutectoid microstructure becomes finer and more uniform with brazing temperature, which is contributed to a certain degree of homogenization of the brazed joint. It is also worth noted that the microstructures on both sides of the brazing seam center are quite different, which is mainly manifested in the presence of a distinct single layer of α-Ti on one side. This is possibly related to the temperature gradient caused by asymmetric equipment conditions of the sample, which promotes the formation of a layer of α-Ti on one side of the brazing seam. And the Ti atoms of the upper substrate are more likely to diffuse downward toward the molten filler metal and accumulate, while the Ti atoms of the underlying substrate upward diffusion are suppressed to some extent.

When the brazing temperature is 890 and 905 °C, the brazed joint contains four zones, and the overall microstructure is obviously inhomogeneous. As the brazing temperature increases, the bulk (Ti, Zr)_{2}(Cu, Ni) intermetallic compound is eliminated,
naturally the zone IV absent, as shown in Fig. 6(c), (d) and (e). The interaction between
the substrate and the filler metal is strengthened, which results in an increase in Ti
concentration in the brazing seam and a decrease in Zr, Cu and Ni. Eventually, the bulk
(Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound absence and the \(\alpha\)-Ti volume fraction
increases. However, a small amount of \(\alpha\)-Ti grows strongly to a flaky shape, as shown
in Fig. 6(e). Another possible reason for the absence of the (Ti, Zr)\(_2\)(Cu, Ni) intermetallic
compound is that the dissolution of the substrate into the filler metal is enhanced, and
the residual filler metal is driven out by the partially molten substrate due to external
pressure. In previous studies \([19, 25]\), further increases in brazing temperature and
extended soaking time to completely eliminate intermetallic compounds in the brazed
joint may also be explained by this guess. However, excessive brazing temperature and
time results in dissolution and corrosion of the substrate \([15, 30]\), especially for the
performance of thin-walled structures. In addition, the excessive brazing temperature
may even cause the substrate to be unapplied \([19]\).

Figure 6(f), (c), (g) and (h) are the microstructures of brazed joints with different
brazing time at 920 °C. The thickness of the brazing seam increased with time and was
62, 105, 106 and 134 μm, respectively. It is shown that the brazing time has a more
severe effect on the mutual dissolution and diffusion of the substrate and the filler metal.
The bulk (Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound exists as shown in Fig. 6(f), which
is eliminated as the holding time increases. The dissolution and diffusion of the filler
metal can also be enhanced with extended holding time. Further prolonging the holding
time, the columnar \(\alpha\)-Ti has adequate conditions for nucleation
and growth, and its volume fraction is significantly increased, due to the continuous diffusion of Ti atoms for a long time and gradually dominates the brazed joint, as shown in Fig. 6(h).

With the increasing of brazing temperature and time, more intense mutual metallurgy acts on the substrate and the filler metal, which eliminates the bulk (Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound and promotes \(\alpha\)-Ti growth. Extending the brazing time results in a sharp increase in the content of columnar \(\alpha\)-Ti, which contributes to the overall homogenization of the brazed joint.
Fig. 6. Interfacial microstructure of brazed joints under different brazing conditions: (a) 890 °C, 10 min; (b) 905 °C, 10 min; (c) 920 °C, 10 min; (d) 935 °C, 10 min; (e) 950 °C, 10 min; (f) 920 °C, 5 min; (g) 920 °C, 20 min; (h) 920 °C, 30 min.
4.3. Fracture analysis of the brazed joint

The strength of the brazed joint is largely based on the microstructure. When the brazing temperature is insufficient, the atomic diffusion and mutual dissolution of the substrate and the filler metal are restricted, which results in lower shear strength. When the brazing temperature is raised, wetting and caulking action of the liquid filler metal is improved to reduce its mismatch with the substrate, so that it can be utilized more efficiently. This is mainly presented in the absence of bulk (Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound, as shown in Fig. 6(c). It is noted that the eutectoid microstructure is finer by comparing the pictures inserted in Fig. 6(a) and (c), which is advantageous for the strength improvement of the brazed joint [6, 16]. Since the fine and uniform distribution of the intermetallic compound on the solid solution matrix can increase the shear strength of the brazed joint. The brazed joint has a maximum shear strength of 486.51 MPa when the brazing temperature is 920°C. However, as the brazing temperature is further raised, the volume fraction of \(\alpha\)-Ti does not change significantly and a small amount of \(\alpha\)-Ti grows vigorously, which is disadvantageous for the release of residual thermal stress of the brazed joint and results in a decrease in the shear strength. The shear strength of the brazed joint increases first and then decreases with brazing temperature, as shown in Fig. 5(a).

With the increasing of brazing time, no bulk (Ti, Zr)\(_2\)(Cu, Ni) intermetallic compound exists, and the columnar \(\alpha\)-Ti content in the brazed joint increases drastically, as shown in Fig. 6(h). The bond strength of the brazed joint is significantly increased due to the release of residual stress. Therefore, the brazed joint achieved a
maximum shear strength of 635.77 MPa when the brazing time was 30 min. The tendency of the shear strengths is consistent with the results in Fig. 5(b). In addition, the practical shear strength is higher due to the inevitable primary fracture of the specimen from a bonding surface. In summary, the elimination of bulk (Ti, Zr)$_2$(Cu, Ni) intermetallic compound and the presence of a massive of columnar α-Ti are necessary to obtain a higher strength of the brazed joint.

Fracture analysis is an effective method for studying crack initiation and propagation in shear testing of brazed joint. Fig. 7 display the typical fracture path and corresponding fracture morphology of the brazed joints under different brazing conditions after room temperature shear testing. When the brazing temperature and time are insufficient, the fine cracks first nucleate in the bulk (Ti, Zr)$_2$(Cu, Ni) intermetallic compound and propagate in the central zone IV due to external conditions. Because the plastic deformation ability of this phase is poor, it is not conducive to the release of residual stress due to the mismatch of thermal expansion coefficients between the substrate and the phase. The fracture position of the brazed joint is initiated in the hard and brittle bulk (Ti, Zr)$_2$(Cu, Ni) intermetallic compound, as shown in Fig. 7(a). This is consistent with many previous studies [5, 22, 23, 31]. With the brazing temperature and time, cracks also tend to sprout and propagate in the central zone until fracture due to the absence of a distinct brittle phase in the brazed joint, as shown in Fig. 7(c), (e) and (g). Furthermore, it can be seen in Fig. 7(c) that a secondary crack appears in zone I, which is relatively weak due to intergranular penetration, although the single α-Ti layer has very good plasticity. Conversely, the
intergranular penetration in Fig. 7(e) is not obvious and there is no secondary crack. It is noted that the firmly bonded brazed joint breaks from a small area of the substrate in Fig. 7(g), which is relatively weak due to the slight over-dissolution and corrosion of the substrate as aforementioned. The partial fracture characteristics of the brazed joint are labeled in Fig. 7(b), (d), (f) and (h), cleavage facets, tear edges and river patterns were found. The fracture mode of the brazed joints is cleavage fracture as shown in Fig. 7(b), and quasi-cleavage fracture is shown in Fig. 7(d), (f) and (h). However, more plastic fracture characteristics are shown in Fig. 7(h). Table 3 shows the main chemical compositions of the reaction products of the fracture surfaces in Fig. 7(b), (d) and (h). The major phase of the fracture surface is consistent with the above analysis. These results were further confirmed by XRD analysis as shown in Fig. 8.
Fig. 7. The fracture position and corresponding fracture morphology of the brazed joints under different brazing conditions after room temperature shear strength test: (a) and (b) 905 °C, 10 min; (c) and (d) 920 °C, 10 min; (e) and (f) 950 °C, 10 min; (g) and (h) 920 °C, 30 min.

Table 3

The chemical compositions (at.%) of different positions in Fig. 7.

<table>
<thead>
<tr>
<th>Spot</th>
<th>Al</th>
<th>Zr</th>
<th>Ti</th>
<th>V</th>
<th>Ni</th>
<th>Cu</th>
<th>Possible phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.72</td>
<td>23.59</td>
<td>36.57</td>
<td>0.94</td>
<td>13.48</td>
<td>16.70</td>
<td>(Ti, Zr)$_2$(Cu, Ni)</td>
</tr>
<tr>
<td>B</td>
<td>09.83</td>
<td>24.79</td>
<td>37.41</td>
<td>0.87</td>
<td>12.30</td>
<td>14.80</td>
<td>(Ti, Zr)$_2$(Cu, Ni)</td>
</tr>
<tr>
<td>C</td>
<td>5.30</td>
<td>10.05</td>
<td>73.82</td>
<td>0.30</td>
<td>4.28</td>
<td>6.24</td>
<td>α-Ti or eutectoid microstructure</td>
</tr>
<tr>
<td>D</td>
<td>6.25</td>
<td>5.78</td>
<td>79.24</td>
<td>2.75</td>
<td>2.16</td>
<td>3.82</td>
<td>α-Ti or eutectoid microstructure</td>
</tr>
<tr>
<td>E</td>
<td>6.28</td>
<td>4.69</td>
<td>81.27</td>
<td>1.70</td>
<td>2.18</td>
<td>3.88</td>
<td>α-Ti or eutectoid microstructure</td>
</tr>
<tr>
<td>F</td>
<td>4.80</td>
<td>3.76</td>
<td>84.92</td>
<td>1.79</td>
<td>1.67</td>
<td>3.06</td>
<td>α-Ti or eutectoid microstructure</td>
</tr>
</tbody>
</table>
Fig. 8. (a), (b) and (c) are the XRD analysis of the fracture surface in Fig. 7(b), (d) and (h), respectively.

5. Conclusions

The TC4 alloy was successfully brazed using Ti-37.5Zr-10Ni-15Cu (wt.%) filler metal. The effect of brazing temperature and time on the microstructure and shear strength of the brazed joint were investigated. Based on the current work, the conclusions summarized are as follows.

(1) When the brazing temperature was 905 °C for 10 min, the typical interfacial microstructure of the brazed joint consists of four zones, mainly composed of a single layer of α-Ti with a high concentration of Ti, α-Ti, bulk (Ti, Zr)₂(Cu, Ni) intermetallic compound and eutectoid microstructure.

(2) Increasing the brazing temperature and time both contribute to the elimination of the bulk (Ti, Zr)₂(Cu, Ni) intermetallic compound in the brazed joint. When the
temperature is further increased, a small portion of α-Ti grows sharply. However, as the holding time is extended, the content of columnar α-Ti is remarkably increased. The microstructure of the brazed joint is primarily due to the diffusion of Ti atoms and partial dissolution of the substrate, which is highly dependent on brazing temperature and time.

(3) The maximum shear strength of the brazed joint reached 635.77 MPa at a brazing temperature of 920 °C for 30 min. Correspondingly, a large volume fraction of α-Ti is present in the brazed joint. Extending the holding time is obviously beneficial to increasing the strength.

(4) When the brazing temperature and holding time are insufficient, the crack tends to initially germinate and propagate in the bulk (Ti, Zr)_{2}(Cu, Ni) intermetallic compound. Secondary crack occurs in the relatively weak intergranular penetration zone I. The fracture modes of the brazed joint are cleavage fracture and quasi-cleavage fracture, which are all brittle fractures.

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