Microstructure and brazing mechanism of TiAl/Ni-based superalloy joints using Ti-Zr-Cu-Ni-Co-Mo-B filler metal with different cooling rates

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Abstract. For the purpose of elevated temperature service and weight reduction in aerospace vehicle applications, a novel Ti-Zr-Cu-Ni-Co-Mo-B filler metal was employed to join TiAl to Ni-based superalloy (GH536). The effect of cooling rate on interfacial microstructure of the joints were analysed by scanning electron microscope and energy dispersive X-ray spectrometer. The representative joint microstructure was primarily composed of six characteristic layers, including TiAl substrate / B2 / τ3 (Al3NiTi2) / τ4 (AlNi2Ti) / Cr-rich (Cr, Ni, Fe)ss, τ4 (AlNi2Ti), Ni-rich (Cr, Ni, Fe)ss and TiNi3) / GH536 substrate. With the decrease of cooling rate in the range of furnace cooling-5 ℃/ min, the joint shear strength firstly increased and then decreased. The joint brazed at 1170 °C for 10 min and cooling to 870 ℃ with 10 ℃/min obtained the maximum shear strength of 252 MPa and the shear fracture mainly occurred in τ3 phase area.

1. Introduction
With attractive properties of relatively low density, high specific strength, excellent creep resistance and good oxidation stability at elevated temperature, TiAl alloy are considered as fascinating light-weight high temperature structural material with wide application prospect [1-3]. Compared with Ni-based superalloy applied in the aviation field, TiAl alloy can significantly reduce the weight of aircraft and improve its launch and flight efficiency [4-5]. Therefore, the dissimilar joining of TiAl alloy to Ni-based superalloy has attracted more and more attention due to its excellent high-temperature properties and the remarkable weight reduction effect.

However, the joining of TiAl alloy to Ni-based superalloy is a enormous challenging because of great differences in physical and chemical properties. First, a large number of Ti-Ni intermetallic compounds are easy to be generated in that the dissolution enthalpy of Ti in liquid Ni solvent is -170 KJ/mol [6]. Besides, the thermal expansion coefficient of TiAl alloy is much smaller than that of Ni-based superalloy. Therefore, the dissimilar joining of TiAl alloy to Ni-based superalloy would easily generate thermal stress cracks and thus deteriorate the joint performance. So that it is very important to suppress the generation of brittle phase and to ensure fine metallurgical quality at the joining interface.

In recent years, a few of studies have been conducted on the brazing of TiAl alloy and Ni-based superalloy with Ti(Zr)-based filler metal. Chen et al. [7] brazed the Ti3Al alloy and GH536 with Ti-13Zr-21Cu-9Ni (wt%) filler metal. However, a lot of intermetallic compounds formed in the brazing joint, which would cause the formation of micro-cracks during cooling process. Thus, the shear strength of the joint is low (only 86 MPa). Furthermore, As reported in ref. [8, 9], increasing Zr content and
controlling Cu and Ni content can effectively reduce the amount of intermetallic compounds in the joint. In addition, adding Co and Mo to Ti-Zr-Cu-Ni filler can improve the high-temperature strength, creep resistance and corrosion resistance of TiAl brazed joints [10].

In order to depress the generation of thermal stress cracks and reduce the amount of intermetallic compounds, a new amorphous filler Ti-23.5Zr-19Cu-14Ni-3Co-2Mo-0.5B (wt%) was employed to braze TiAl alloy and Ni-based superalloy (GH536). The microstructure of the dissimilar joint were analyzed in details. The effects of cooling rate on the microstructural and the mechanical properties of the joints were also investigated.

2. Materials and experimental procedures

The chemical compositions of TiAl alloy and GH536 used in this study are listed in Table 1. Amorphous filler with a nominal composition of Ti-23.5Zr-19Cu-14Ni-3Co-2Mo-0.5B (wt%) was produced by rapid solidification technology in a vacuum single roller spinning quenching system. The obtained foil was 10 mm wide and 40 µm thick. The structure of the foil was examined by X-ray diffraction (XRD), the result was shown in Fig. 1(a), respectively. It can be seen from Fig. 1(a) that there is only one coarse diffusion diffraction peak, which proved foil is entirely amorphous. Looking up and comparing PDF cards through jade software shows that the phase of amorphous filler is β-(Ti, Zr).

Brazing experiments were carried out with 6 mm×5 mm×3 mm TiAl alloy and 22 mm×6 mm×3 mm GH536. All contacting surfaces were polished by the SiC paper to 800 grit and cleaned ultrasonically in absolute ethyl alcohol. Then, the brazing foil was placed between the TiAl and GH536 specimens to form sandwich structure, as shown in Fig. 1(b). The brazing experiments were carried out at HP-12×12×12 heating furnace with vacuum level up to 1.33×10^{-2} Pa, and the brazing heating curve is illustrated in Fig. 2. At the beginning of brazing process, the furnace was initially heated to 200 ℃ at a rate of 10 ℃/min. Afterward, a higher heating rate of 20 ℃/min was employed to heat the samples to 1170 ℃ and maintained for 10 min. Eventually, the specimens were cooled down to 870 ℃ at different rates and then cooling to room temperature in the furnace.

| Table 1 Average chemical composition of TiAl and GH536 (at%). |
|-----------------|-------|-----|-----|-----|-------|-----|-----|-----|
|                 | Al    | Ni  | Cr  | Ti  | Nb    | Fe  | Co  | Mo  | W    |
| TiAl            | 43.69 | —   | 2.71| Bal | 2.38  | —   | —   | —   | —    |
| GH536           | 0.40  | Bal | 25.65| —   | —    | 18.47| 2.05| 5.30| 0.24 |

After brazing, the joint microstructures were characterized by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDS). The shear tests were conducted using a Shimadzu AG-X100KN Universal Material Testing Machine to evaluate the bonding strength of the brazed joints. The brazed joints was compressed with a constant loading rate of 0.5 mm/min at room temperature and the average shear strength of different brazing conditions was obtained from five brazed joints.

![Fig. 1. (a) XRD pattern of the filler metal; (b) Schematic diagram for joining experiment.](image-url)
3. Result and discussion

3.1. Microstructure of the brazed joint

Fig. 3 shows the SEM images of the joints brazed at 1170 °C for 10 min and cooling to 870 °C at 10 °C/min. Brazed joints are well formed and free of defects such as pores and micro-cracks. As shown in Fig. 3(a), it can be clearly seen that the brazed joint can be divided into four layers (marked by I, II, III and IV, respectively) based on the microstructural morphology and the chemical composition. And Fig. 3(b) and (c) illustrates the magnified microstructures of layers I-IV. To verify the phase constitution in each layer, EDS analysis was carried out on the microstructure of the brazed joints, and the EDS results were listed in Table 2.

![Fig. 2. Heating curve for the brazing process.](image)

**Table 2** The chemical compositions (at%) of different positions in Fig. 3.

| Spot | Ti  | Al  | Ni  | Cr  | Fe  | Zr  | Cu  | Nb  | Co  | Mo  | Possible phase                  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|---------------------------------|
| Layer I |     |     |     |     |     |     |     |     |     |     |                                 |
| Layer II | 56.07 | 35.07 | 1.51 | 3.51 | 0.98 | 0.00 | 0.06 | 2.50 | 0.07 | 0.14 | B<sub>2</sub>                    |
| Layer III | 33.51 | 39.71 | 17.43 | 3.42 | 3.41 | 0.00 | 0.34 | 1.81 | 0.32 | 0.06 | τ<sub>3</sub>                   |
| Layer IV | 16.19 | 24.41 | 46.67 | 4.24 | 5.62 | 0.41 | 0.55 | 0.32 | 1.24 | 0.35 |                                 |
| A    | 6.93 | 6.63 | 43.01 | 18.80 | 18.80 | 0.24 | 0.97 | 0.19 | 1.79 | 2.63 | Cr-rich (Cr, Ni, Fe)<sub>ss</sub> |
| B    | 16.88 | 20.53 | 47.55 | 5.02 | 5.58 | 0.90 | 0.96 | 0.44 | 1.49 | 0.66 | Ti<sub>4</sub>                  |
| C    | 18.37 | 4.15 | 63.39 | 3.81 | 5.96 | 1.28 | 0.69 | 0.23 | 1.74 | 0.38 | Ni-rich (Ni, Cr, Fe)<sub>ss</sub> |
| D    | 3.34 | 2.68 | 19.22 | 40.26 | 19.86 | 0.30 | 0.20 | 0.06 | 1.74 | 12.34 | Cr-rich (Cr, Ni, Fe)<sub>ss</sub> |
As shown in Fig. 3(b), a continuous interface reaction layer I is formed between TiAl alloy and brazing seam, and the formation of layer I is the basis for realizing chemical metallurgical connection between TiAl alloy and brazing seam. According to Table 2, layer I is mainly composed of Ti, Al atoms and some β-Ti stable elements. Combined with Ti-Al binary phase diagram [11], indicating that layer I was B2 phase. Layer II is an isothermal solidification layer at TiAl-side. According to the EDS results, layer II and layer III are mainly composed of Ti, Ni and Al atoms. Furthermore, the Al and Ti contents in layer II is higher, and the Ni content in layer III is higher. Thus, combined with Ti-Ni-Al ternary alloy phase diagram [12], layer II can be judged to be Al3NiTi2, that is, the τ3 phase. Layer III can be deduced to be the AlNi2Ti phase, namely τ4 phase.

The white matrix phase A in layer IV is mainly composed of Cr, Fe and Ni, and the atomic ratio of Cr,Fe and Ni is close to 2:1:1, which is inferred as Cr-rich (Cr, Ni, Fe)ss phase (ss represents solid solution). The gray phase B between layer III and layer IV is primarily composed of Ni and Ti, and the atomic ratio of Ni and Ti is 3:1, which is inferred as TiNi3 according to the Ti-Ni binary phase diagram. The amount of charcoal grey phase C is less but evenly distributed in layer IV, and its composition and atomic ratio are similar to those of layer III, namely is τ4. The light grey phase D is distributed in islands in layer IV and it is primarily composed of Ni, Cr, Fe elements. In addition, the atomic ratio of Ni, Fe and Cr is close to 2:1:1, which is inferred as Ni-rich (Ni, Cr, Fe)ss phase.

3.2. Effect of cooling rate on the interfacial microstructure of the joints

Fig. 4 shows the microstructure of the joints brazed at 1170 °C for 10 min and cooling to 870 °C with furnace cooling, 10 °C/min, 7.5 °C/min, 5 °C/min, respectively. When the cooling method is furnace cooling, the cooling rate at high temperature (higher than 870 °C) is about 12.5 °C/min by measurement and calculation, and the cooling rate slows down as the temperature decreases. As shown in Fig. 4(a), it can be seen that there are many micro-cracks between in the layer I and layer II. This is mainly due to the remarkable inhomogeneity of the microstructure on both sides of the brazing seam, the formation of more intermetallic compound phases and the thermal stress in the brazing cooling process. When the cooling rate is slowed to 10 °C/min, the reaction time between the filler metal and the base metal is prolonged, so that the metallurgical reaction become sufficient, the joints are well formed and free of defects such as pores and micro-cracks, as shown in Fig. 4(b). Furthermore, due to the cooling rate become slow, the generation of thermal stress cracks are inhibited. As can be seen from the Fig. 4(c) and (d), the thickness of the brazing seam become obviously narrower as the cooling rate drops to 7.5 °C/min and 5 °C/min. In addition, as the cooling rate decreases, Cr-rich (Cr, Ni, Fe)ss in the layer IV becomes coarse, the amount of τ4 phase and Ni-rich (Ni, Cr, Fe)ss phase decrease.
Fig. 4. Effect of cooling rate on microstructure of TiAl/GH536 joints brazed at 1170 °C for 10 min.

Fig. 5 shows the change trend of brazing seam thickness and interfacial reaction layer thickness with different cooling rates. Actually, the thickness of the brazing seam mainly affected by the dissolution of the base metal and the loss of filler. The dissolution of the base metal on both sides will increase the thickness of the brazing seam, and the loss of filler at elevated temperature will play a role in reducing [13]. As the cooling rate slows down, the duration of brazing at high temperature becomes longer, and the loss of brazing filler metal increases, resulting in a narrower brazing seam thickness. In addition, the loss of filler leads to the reduction of the thickness of layer IV, while the change of the thickness of layer I, II, III is not obvious.

Fig. 5. Effect of cooling rate on the thickness of brazing seam and reaction layers.
3.3. Mechanical properties and fracture morphology

Fig. 6 displays the room temperature shear strength of the joints brazed at 1170 °C for 10 min and cooling to 870 °C with furnace cooling, 10 °C/min, 7.5 °C/min, 5 °C/min, respectively. It can be seen from the figure that with the decrease of cooling rate, the shear strength first increases and then decreases. When the cooling method is furnace cooling, the brazed joint has obvious micro-cracks, resulting in low shear strength (237 MPa). When the cooling rate is 10 °C/min, the joints is well formed and without pores and micro-cracks defects, the shear strength of the joint is the highest, reaching 252 MPa. However, when the cooling rate slows to 7.5 °C/min and 5 °C/min, due to loss of the filler, resulting in thinner brazing seam, increasing residual stress in joint brazing seam. Thus, the shear strength decreased to 245 MPa and 219 MPa, respectively.

According to aforementioned analysis, the interfacial morphologies and phase compositions in each layer of the other joints are almost similar, but the maximum shear strength of the brazed joint is obtained with cooling rate of 10 °C/min. Therefore, the shear fracture path and fracture morphology of the TiAl/GH536 joint with cooling rate of 10 °C/min is selected to study and the corresponding SEM images were shown in Fig. 7. It can be seen that the fracture area of the joint is located in layer II, and the fracture surface exhibited a cleavage fracture with river pattern. EDS analysis was carried out on the fracture surface, and results were listed in Table 3. It can be seen that the fracture surface is \( \tau_3 \) intermetallic compound. Accordingly, it is inferred that the layer II primarily consisted of brittle \( \tau_3 \) intermetallic compound is the weakest area in the brazing seam.

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![Fig. 6. Effect of cooling rate on the thickness of brazing seam and reaction layers.](image)

![Fig. 7. (a) Fracture location; Fracture morphology of the joint brazed at 1170 °C for 10 min and cooling to 870 °C with 10 °C/min.](image)
Table 3 The chemical compositions (at%) of different positions in Fig. 7(b).

| Spot | Ti  | Al  | Ni  | Cr  | Fe  | Zr  | Cu  | Nb  | Co  | Mo  | Possible phase |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----------------|
| A    | 35.72 | 37.45 | 16.95 | 3.44 | 3.22 | 0.00 | 1.67 | 0.56 | 0.08 |     | τ₃            |
| B    | 30.80 | 42.60 | 16.22 | 3.22 | 3.54 | 0.10 | 0.83 | 1.99 | 0.44 | 0.25 | τ₃            |

4. Conclusions
(1) Vacuum brazing of TiAl alloy to GH536 alloy was successfully achieved by using Ti-Zr-Fe-Cu-Ni-Co-Mo filler metal.
(2) The typical microstructure of the joint brazed at 1170 °C for 10 min and cooling to 870 °C with 10 °C/min was confirmed to be TiAl substrate / B2 / τ1 (Al3NiTi2) / τ4 (AlNi2Ti) / Cr-rich (Cr, Ni, Fe), Ni-rich (Ni, Cr, Fe), τ4 (AlNi2Ti) and TiNi3 / GH536 substrate.
(3) As the cooling rate decreased, the thickness of the brazing seam and layer IV decreased, while the change of the thickness of layer I, II, III is not obvious. The shear strength of the joints increased first and then decreased with the decrease of the cooling rate. The joint brazed at 1170 °C for 10 min and cooling to 870 °C with 10 °C/min obtained the maximum shear strength of 252 MPa. Brazed joints were mainly broken in layer II. The fracture surface shows typical cleavage fracture characteristic.

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