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Brazing of Ti_2AlNb Based Alloy with Amorphous Ti-Cu-Zr-Ni Filler

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Abstract: Amorphous Ti-Cu-Zr-Ni filler foils with low melting point of 1 133 K were synthesized using a melt-spinning method in argon atmosphere. A Ti_2AlNb based alloy was brazed at 1 153-1 223 K for 600-3 000 s. The effects of brazing temperature (T_b) and time (t_b) on the shear strength of the joints were investigated. The results showed that the joint strength was significantly affected by the reaction layer thickness. The optimum brazing parameters can be determined as follows: T_b=1 173 K, and t_b=600 s. The maximum tensile strength of the joint obtained can reach 260 MPa. Furthermore, the activation energy Q and the growth velocity A_0 of the reaction layer in the brazed joints were calculated to be 161.742 kJ/mol and 0.213 m^2/s, respectively. The growth of the reaction layer (y) could be expressed by the expression: $y^2 = 0.213\exp(-19\,454/T_b)t_b$.

Key words: brazing; Ti_2AlNb; amorphous filler; reaction layer

1 Introduction

Amorphous alloys, as a kind of metastable materials, can accelerate atomic diffusion and surface reaction during high temperature brazing process. In addition, it is expected that the decrease in brazing temperature can reduce the residual stress developed in the joint and hence increase the joint strength[1-3]. Since the first amorphous filler alloy patent was applied by D'Silva in 1979, amorphous filler alloys have attracted increasing attention in the fields of ceramic/ceramic[4,5], metal/metal[6-8] and ceramic/metal[9-12] joining owing to their unique properties, instead of crystalline alloy fillers. Zou *et al* reported that amorphous $Ti_{40}Zr_{25}Ni_{15}Cu_{20}$ demonstrated a better wettability than crystalline $Ti_{40}Zr_{25}Ni_{15}Cu_{20}$ on Si_3N_4 ceramic. The strength of joint brazed with amorphous $Ti_{40}Zr_{25}Ni_{15}Cu_{20}$ filler was significantly affected by the reaction layer thickness, reaching a maximum strength of 160 MPa[4]. He *et al* studied the weldability of Ti_3Al alloys with the amorphous filler metal Ti–Zr35–Ni15–Cu15 (wt%). The relationship between the brazing parameters and shear strength of the joints was discussed and the optimum brazing parameters were obtained. The maximum shear strength of the joint is 250 MPa[8]. Liu *et al* reported that the joining of SiO_2 glass ceramic and Ti–6Al–4V alloy was successfully realized by using AgCuTi filler foil. The microstructure of the brazed joint was discussed in detail. When the joint was brazed at 900 ℃ for 5 min, the maximum shear strength can reach 27 MPa[11].

It is well known that Ti_2AlNb based alloy has promising properties such as high specific strength, high creep resistance, excellent high temperature mechanical properties and good inoxidizability, which is considered to be a favorable structural material with potential application in spacecraft and aircraft[13,14]. However, the manufacturing cost of the Ti_2AlNb-based alloys is too high, which severely limits their further development. Therefore, joining of these alloys is an indispensable processing method. Among the joining methods, brazing has been considered to be one of the most effective joining methods due to its simplicity, low costs, good repetitiveness as well as perfect adaptability of joint size and shape. To date, there are

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some reports on the joining of Ti_2AlNb based alloy by laser beam welding[15-17]. However, few attempts have been dedicated to study the brazing of Ti_2AlNb based alloy by amorphous filler.

In this paper, rapid solidification technology was utilized to fabricate TiCuNiZr amorphous brazing foils, with which the Ti_2AlNb based alloy was brazed under different parameters. The joints with different thickness of reaction layer were obtained. The relationship between the reaction layer thickness and strength of the Ti_2AlNb-Ti_2AlNb joints was established.

2 Experimental

Amorphous $Ti_{30.21}Cu_{41.83}Zr_{19.76}Ni_{8.19}$ (at%) alloy foils were prepared by remelting the alloy ingot in quartz tubes and ejecting through a nozzle onto a copper wheel rotating at a velocity of 40 ms^{-1} in a purified argon atmosphere. The melting point of foil was 1 133 K, which was detected by differential scanning calorimeter (DSC). The thickness of this foil was 30 μm. The structure of the fabricated brazing foil was examined by X-ray diffraction (XRD) using Cu Kα radiation. The Ti_2AlNb alloy sample used in this investigation was fabricated by vacuum melting. The nominal compositions of Ti_2AlNb based alloy material are given in Table 1.The size of the Ti_2AlNb sample for brazing was 3 mm×3 mm×17 mm. Before joining, the brazing surface was carefully polished.

Table 1 Nominal chemical compositions of Ti_2AlNb based alloy

Element	Ti	Al	Nb	V	Mo	Si
Content/at%	53.38	10.62	32.48	1.71	1.65	0.16
Content/wt%	58.24	20.55	18.26	1.75	0.89	0.29

The brazing temperature was from 1 153 to 1 223 K and the brazing time was from 600 to 3 000 s. During the brazing process, a pressure of 0.016 MPa was exerted on the brazing sample to ensure each part contact closely. The brazing process was conducted in a vacuum of 1×10^{-3} Pa. At the beginning, the brazing sample was heated up to 573 K at a rate of 10 K/min and held steady for 20 min to make the organic glue volatilize and to keep the brazing surfaces clean. Then the temperature was increased to the brazing temperature at a rate of 10 K/min and held constant for different brazing times. At last, the brazing sample was cooled down at a rate of 5 K/min to 573 K and then cooled freely in the furnace.

After joining, the microstructure and composition of the joint were examined by scanning electron microscopy (SEM, Quanta 200FEG) with energy-dispersive X-ray spectrometer (EDS) and micro-area X-ray diffraction (XRD, Bede D1) with the X-ray beam with 50 μm diameter. The tensile strength of the joint was measured by using an Instron 5500 testing machine at a compression strain rate of 1×10^{-4} s^{-1} at room temperature.

3 Results and discussion

Fig.1 shows a typical X-ray diffraction pattern taken from $Ti_{30.21}Cu_{41.83}Zr_{19.76}Ni_{8.19}$ alloy foils. There was only a broadened diffraction peak on the curve and no obvious sharp diffraction peak corresponding to any crystallization could be observed, indicating the amorphous nature of the brazing filler metal.

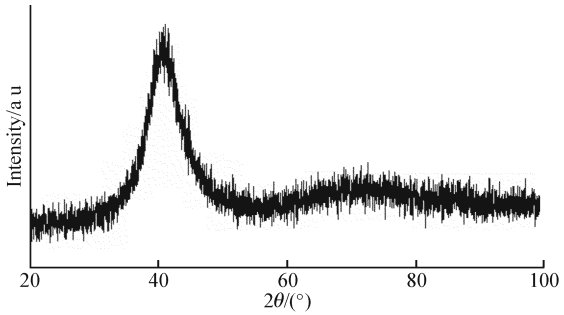

Fig.1 XRD pattern of the $Ti_{30.21}Cu_{41.83}Zr_{19.76}Ni_{8.19}$ filler alloy

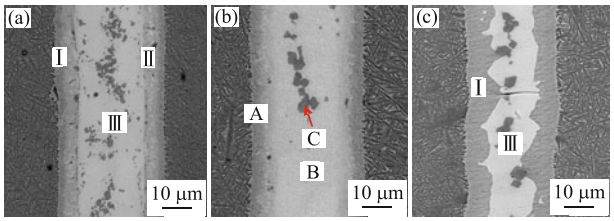

Fig.2 SEM images of joint interface brazed at (a) 1 153 K; (b) 1 173 K; (c) 1223 K for 600 s

Fig.2 shows the microstructure of the cross-sections of the Ti_2AlNb/TiCuNiZr/Ti_2AlNb joints brazed at brazing temperatures ranging from 1 153 to 1 223 K for the brazing time of 600 s. As seen, two kinds of reaction layers take place between Ti_2AlNb based alloy and TiCuZrNi. Also, the interface between the matrix and filler display rugged. The distribution of elements at the brazed Ti_2AlNb/TiCuNiZr interface shows that atomic diffusion occurred between Ti_2AlNb based alloy and TiCuZrNi alloy foils. The reaction layer with the grey phase adjacent to Ti_2AlNb based alloy, in the middle, and with some black block phase in the white base is called as layer I, layer II, and layer

III(B+C), respectively From Fig.2, we can see that with the increasing in the brazing temperature, the layer II becomes indiscernible. When temperature increases to 1 223 K, the layer II disappears and the size of layer I increases into 10 μm, while the size of black block phase increases in the layer III. Also, the transverse crack is observed when the brazing temperature is 1 223 K, which maybe results in the low joint strength.

Table 2 Average contents of major element in each reaction layer/phase of the Ti_2AlNb/TiCuZr–Ni/Ti_2AlNb joint brazed at 1 173 K for 600 s (at%)

Location	Ti	Cu	Zr	Ni	Al	Nb
A	55.15	5.93	2.08	1.28	14.91	20.66
B	32.54	33.93	16.33	7.64	6.70	2.87
C	59.12	29.39	3.76	3.68	0.65	3.40

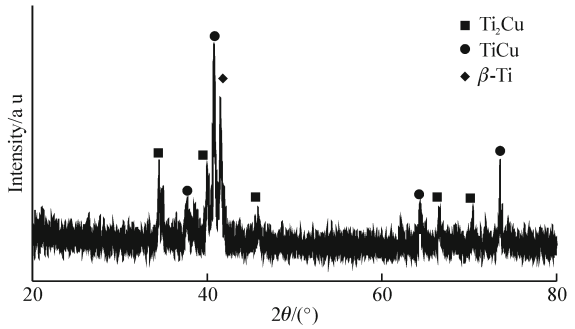

Fig.3 Micro-area XRD patterns from the joint interface of the Ti_2AlNb/TiCuNiZr/Ti_2AlNb joints brazed at 1 173 K for the brazing time 600 s

Table 2 shows the EDS chemical analysis results of the Ti_2AlNb/TiCuNiZr/Ti_2AlNb joints brazed at 1 173 K for a brazing time of 600 s. The distribution of elements at the brazed Ti_2AlNb/TiCuNiZr interface shows that a certain amount of diffusion occurred between Ti_2AlNb based alloy and TiCuZrNi alloy foils. The layer I or II was mainly composed of Ti, Al and Nb elements, in which the proportion of Ti, Al and Nb is similar to that of the Ti_2AlNb based alloy. In the layer III (B+C), the elements Ti and Cu aggregated in the black block phase (C), the proximate proportion of Ti and Cu is 2:1. The white base phase (B) contains similar amounts of Ti and Cu, while the Zr content is much higher than that of the phases A and B, the approximate proportion of Ti, Cu and Zr is 2:2:1. Fig.3 shows the micro-area X-ray diffraction pattern of the cross-sections of the Ti_2AlNb/TiCuNiZr/Ti_2AlNb joint brazed at 1 173 K for a brazing time of 600 s. From the results, the phases formed at the brazed joint are β-Ti, Ti_2Cu and TiCu. Based on Table 2, micro-area XRD results and Ti-Cu-Ni phase diagrams, the phases A, B, and C can be identified as β-Ti, TiCu, and Ti_2Cu, respectively. Therefore, the structure of brazed joints is composed of Ti_2AlNb/β-Ti/Ti_2Cu+ TiCu/β-Ti/Ti_2AlNb.

Fig.4 shows the effect of interface reaction layer thickness on the strength of the joints brazed with different parameters. When the brazing temperatures are 1 153 and 1 223 K, firstly, the tensile strength increases with the increase in reaction layer thickness, then the value drops quickly with increasing holding time. As for the 1 173 K brazing

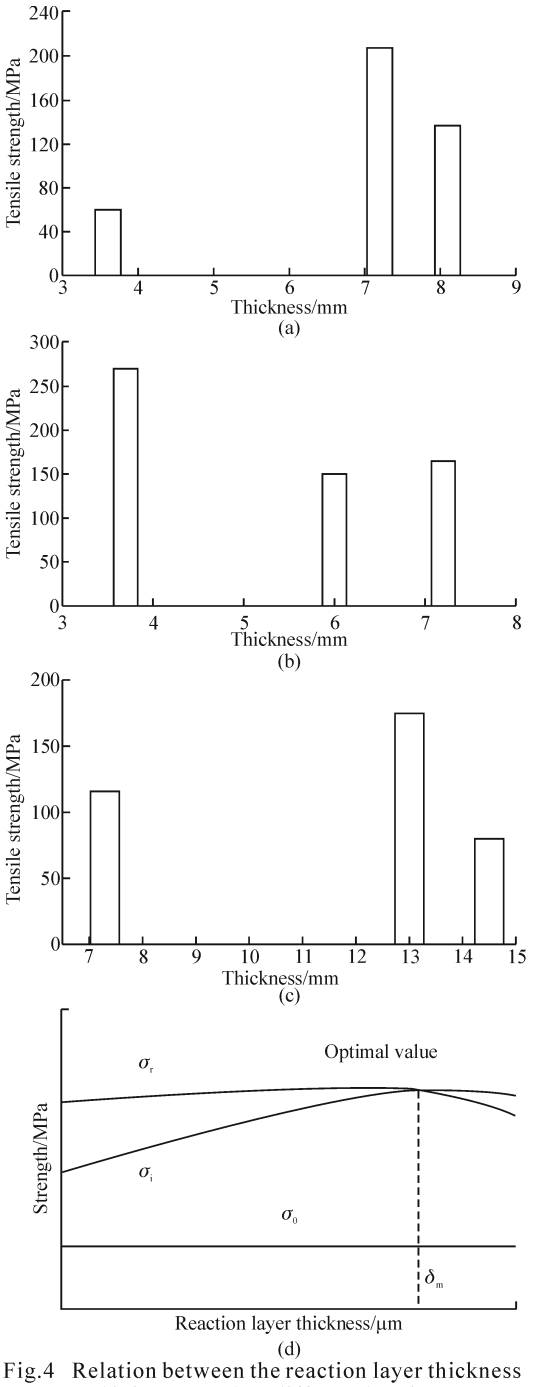

Fig.4 Relation between the reaction layer thickness and joint strength at different brazing temperatures: (a) 1 153 K, (b) 1 173 K, (c) 1 223 K for 600, 1 800 and 3000 s, respectively; (d) Relationship diagram between reaction layer thickness and joint strength

temperature, the joint strength decreases from 260 to 150 MPa as the holding time increases from 600 to 1 800 s. In the present work, the optimum strength of joint (260 MPa) is not only better than that of the joint brazed by the crystalline filler, but also better than that of the joint brazed by the other amorphous filler. For example, the joining of SiO_2 glass ceramic and Ti–6Al–4V alloy was successfully realized by using AgCuTi filler foil. However, the maximum shear strength can reach only 27 MPa[11]. The strength of joint brazed with amorphous $Ti_{40}Zr_{25}Ni_{15}Cu_{20}$ filler on Si_3N_4 ceramic was 160 MPa[4]. The maximum shear strength of the joint brazed with the amorphous filler metal Ti–Zr35–Ni15–Cu15 (wt%) on Ti_3Al alloys was 250 MPa[8]. From Fig.4, it can be speculated that the reaction layer thickness exerts a crucial role on the joint strength. The strength of joint is a comprehensive physical quantity determined by many factors such as coefficient of liner expansion, the performance of brazing filler alloy, brazing parameters and so on. These factors result in the different values of residual stress, interfacial strength and reaction layer strength, ultimately influencing the joint strength. Nakao *et al*[18] have proposed that though the thickness of reaction layer was changed, the residual stress held a constant, meaning that the effect of interface reaction layer thickness on the joint strength was due to the interfacial strength and interfacial reaction layer strength. In the present work, a relationship diagram has been drawn to discuss the influence of reaction layer thickness δ on interfacial strength σ_i, reaction layer strength σ_r and residual stress σ_0, as shown in Fig.4(d). Under certain brazing temperature, the thickness of reaction layer increases with increasing holding time. The interfacial strength increases dramatically due to the intensified interfacial reaction, but the residual stress remains constant. When the reaction layer thickness δ attains the optimal value (δ_m), interfacial strength achieves an optimal value. When further increasing the thickness of reaction layer, the interfacial strength shows slow upward trend, while the reaction layer strength drops sharply. These outcomes are in good agreement with the analysis mentioned above. So here, the reaction layer thickness δ has the best value δ_m, when the reaction layer thickness δ is less than δ_m. The joint strength is controlled by the difference between interfacial strength σ_i and residual stress σ_0. On the other hand, once the reaction layer thickness δ is larger than δ_m, the joint strength is determined by the difference between the reaction layer strength σ_r and residual stress σ_0. So, in the applications, the sufficient interfacial reaction must be ensured, but the preservation time should be controlled precisely. Yoshikuni also discussed the relationship between the interfacial reaction layer thickness and defect and considered that for the thin interfacial reaction layer, no defect was observed. On the contrary, numerous defects such as cracks and pores appeared in the thick reaction layer. In this case, the joint strength (σ) and defects size (a) would meet the conditions:

$$\sigma=k(\pi a)^{-n} \tag{1}$$

where k and n are constants. With the analysis mentioned above, at brazing temperature of 1 153 K for the brazing time of 600 s, the maximum joint strength can be attributed to two aspects. Firstly, based on these parameters, the reaction layer thickness was about 5 μm which was the optimal value of reaction layer thickness in the present work, as shown in Fig.2. With increasing T from 1 153 to 1 223 K, the atomic diffusivity increases which results in an easier and more speedy diffusion reaction and chemical joining. Therefore, the shear strength of the brazed joint increases with increasing T. When T is 1 173 K, the shear strength of joint is a maximum (260 MPa). Secondly, no defect was observed in the reaction layer for 1 173 K and 600 s. However, numerous cracks can be observed in the thick reaction layer, such as 1 173 K for 1 800 and 3000 s, as shown in Fig.5. Combining the results in the present work as shown in Fig.5, the rapid decline in tensile strength was attributed to the thick reaction layer, which gave rise to the emergence of cracks.

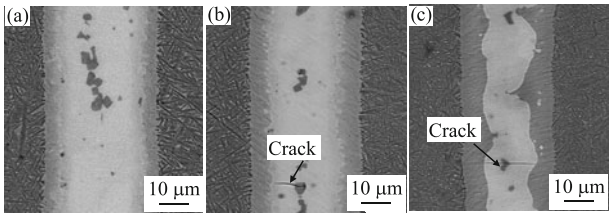

Fig.5 SEM images of joint interface brazed for (a) 600 s, (b) 1 800 s, (c) 3000 s at 1 173 K

To some extent, the thickness of reaction layer was determined by the welding temperature and welding time. He *et al*[8] have pointed out that the growth of the reacting layer in the brazed joint increases with holding time according to a parabolic law, which can be expressed by the equation:

$$y^2=At \tag{2}$$

$$A = A_0 \exp\left(\frac{-Q}{RT}\right) \tag{3}$$

where y is the thickness of the reaction layer, m; t is the bonding time, s; T is the bonding temperature, K; A is the growth velocity of the reaction layer, m^2/s; A_0 is the growth constant, m^2/s; Q is the activation energy, kJ/mol; R is the gas constant, 8.314(J/K mol). From the equation, the activation energy Q and the growth velocity A_0 of the reaction layer in the brazed joints of Ti_2AlNb based alloy with Ti-Zr-Ni-Cu amorphous filler metal can be calculated to be 161.742 kJ/mol and 0.213 m^2/s, respectively. With above analysis, the growth of reaction layer is expressed by the following formula:

$$y^2 = 0.213 \exp\left(\frac{-19\,454}{T}\right)t \tag{4}$$

By virtue of this formula, the growth of the reaction layer can be controlled to improve the bonding strength.

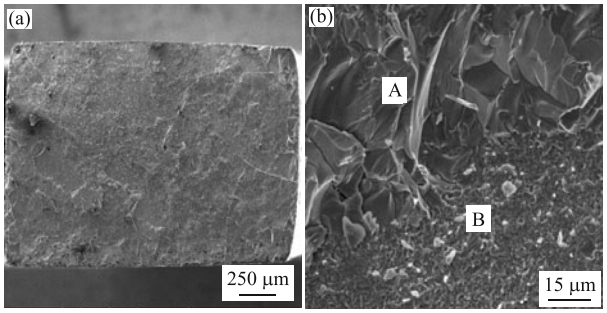

Fig.6 (a) SEM image of whole fracture surface and (b) magnified SEM image at 1 173 K for 600 s

Table 3 EDS analysis of the fracture surface at 1 173 K for 600 s

Area	Ti	Cu	Zr	Ni	Al	Nb
A	36.97	33.82	12.78	5.35	6.60	4.48
B	61.90	3.27	4.01	2.75	10.04	18.03

Fig.6 shows the SEM images of the whole fracture surface and the magnified image at 1 173 K for 600 s, respectively. Their fractured surfaces revealed a quasi-cleavage and plane fracture, as shown in Fig.6(b), revealing the brittleness of the joints. Table 3 shows EDS analysis from the area A and B of the fracture surface at 1 173 K for 600 s. It can be seen that the fracture occurs partially at the middle layer with Ti_2Cu + TiCu intermetallic compounds (area A) and partially at the reaction layer of β-Ti (area B).

4 Conclusions

In summary, we present amorphous Ti-Cu-Zr-Ni filler foils to braze Ti_2AlNb baseed alloy at 1 153-1 223 K for 600-3 000 s. The bonding strength can be improved up to 260 MPa at 1 173 K for 600 s. Three kinds of products were observed in joint interface, namely, β-Ti, Ti_2Cu and TiCu intermetallic compounds. The reaction layer thickness and joint strength have a certain relationship: when the reaction layer thickness is less than primary value, the joint strength is determined by interfacial strength and residual stress; on the contrary, the joint strength is determined by the reaction layer strength and residual stress. Also, the growth of reaction layer has be calculated as: $y^2 = 0.213\exp(-19454/T_b)t_b$. Therefore, through changing the brazing parameters, the thickness of reaction layer can be well controlled, and then an enhanced joint strength can be achieved. From the fracture configuration of 1 173 K for 600 s, the fracture penetrates the whole reaction layer.

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