Note

Microstructural Observation of Brazed Ti-15-3 Alloy Using the Clad Ti-20Zr-20Cu-20Ni Foil

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1. Introduction

Titanium and its alloys are featured with high specific strength as well as good corrosion resistance, and they are particularly suitable for aerospace and medical applications.^{1–3)} Ti-15-3 is a metastable beta titanium alloy that was developed to reduce the strip processing cost due to its excellent forming characteristics at room temperature.^{2,4)} Chemical composition of Ti-15-3 alloy in weight percent is 15%V, 3%Cr, 3%Al, 3%Sn and balance Ti. The strengthening mechanism of Ti-15-3 is attributed to uniformly dispersed fine α precipitates in the β -Ti matrix.

Developing joining process is usually important in the application of many engineering alloys.⁵⁾ Brazing is one of important joining methods applied in industry. Selection of filler metal in brazing titanium alloy is crucial. Ag-based braze alloys are suffered from low bonding strength and poor corrosion resistance.^{6–9)} Clad Ti–Cu–Ni brazing foils demonstrate excellent bonding strength and corrosion resistance as compared with those of Ag-based fillers in brazing many titanium alloys.⁶⁾ Microstructural evolution and phase identification of Ti–Cu–Ni filler brazed joints are unveiled in previous studies.^{4,10–12)} Ti–15Cu–15Ni in wt% is one of the most popular Ti-based filler metals in brazing titanium alloy, and it shows excellent bonding performance after brazing.^{13,14)} Ti-15-3 is a type of β -Ti, and its β transus temperature is 770°C.¹⁾ However, the brazing temperature of Ti–15Cu–15Ni filler metal exceeds 950°C. High brazing temperature results in coarsening the grain size of Ti-15-3 substrate and deteriorating its mechanical properties.

Brazing temperatures of the Ti–Cu–Ni filler metals are further depressed by alloying of Zr into Ti–Cu–Ni fillers. For example, the solidus and liquidus temperatures of Ti–20Zr–20Cu–20Ni (wt%) braze alloy are 842 and 848°C, which are much lower than those of Ti–15Cu–15Ni (wt%) filler, 902 and 932°C.⁵⁾ Because the brazing temperature of Ti–Zr–Cu–Ni filler is below 900°C, coarsening effect of Ti-15-3 substrate is abated during brazing. Based on previous study, the presence of Ti–Cu–Ni intermetallic compounds deteriorates bonding strengths of Ti–15Cu–15Ni and Ti–15Cu–25Ni brazed joints.¹⁵⁾ The brittle Ti–Cu–Ni intermetallic compounds can be completely dissolved into the Ti-rich matrix, and the ductile Ti-rich matrix dominates entire joint under proper brazing conditions. In contrast, few literatures have been focused in characterizing the Ti–20Zr–

20Cu–20Ni brazed joint.

The feasibility of brazing Ti-15-3 using Ti–20Zr–20Cu–20Ni filler in order to produce plate heat exchanger used in corrosive environment needs further study. The purpose of this investigation is concentrated on vacuum brazing Ti-15-3 alloy using the Ti–20Zr–20Cu–20Ni foil. Compared with the traditional furnace brazing, infrared brazing is suitable in studying the microstructural evolution of the joint with the advantage of its rapid heating rate as high as 50°C/s.¹⁵⁾ Both infrared and traditional furnace brazing were performed in the experiment for comparison's purpose. Microstructural evolution, phase identification and interfacial reaction of the brazed joint are extensively assessed in the experiment.

2. Experimental Procedure

Base metals used in the experiment were Ti-15-3 plates with the diameter of 10×10 mm² and 0.4 mm in thickness. All joined surfaces were ground by SiC papers up to grit 1000 and then ultrasonically cleaned by acetone prior to brazing. Clad Ti–20Zr–20Cu–20Ni foil with the thickness of 50 μ m was chosen as the braze alloy.¹⁶⁾ Traditional vacuum brazing was performed under the vacuum of 5×10^{–5} mbar. The heating rate was set at 0.5°C/s throughout the experiment. Infrared brazing was performed using the ULVAC SINKO-RIKO RHL-816C furnace with the vacuum of 5×10^{–5} mbar. The heating rate was set at 10°C/s throughout the experiment. All specimens were preheated at 750°C for 300 s prior to brazing in order to equilibrate temperature profile of the specimen. Phase identification of the joint was performed by furnace brazing at 870°C for 1800 s. Microstructural evolution of brazed joints was evaluated by infrared brazing at 850, 890 and 910°C for 1800 s, respectively.

Cross-sections of joints after brazing were cut by a low-speed diamond saw and subsequently examined by using a JEOL 8600SX electron probe microanalyzer (EPMA) equipped with the wavelength dispersive spectroscopy (WDS). The operation voltage was 15 kV, and the minimum spot size was 1 μ m. For the detailed microstructural observation, transmission electron microscope (TEM) specimens were sectioned in thin slices within brazed zones of the joint. Thin foils were prepared by a standard twin jet-polisher using an electrolyte of 10% HClO₄, 90% C₂H₅OH at –40°C. The operation voltage of twin jet-polisher was kept at 30 V, and its current was 35–40 mA. Thin foil specimens were examined using a Philips TECNAI G² TEM operated at 200 kV. It was equipped with an energy dispersive spectroscopy (EDS) for chemical analysis of specific location in the joint.

3. Results and Discussion

Figure 1 shows microstructural observations and EPMA chemical analysis results of the traditional furnace brazed Ti-15-3/Ti–20Zr–20Cu–20Ni/Ti-15-3 joint at 870°C for 1800 s. Figures 1(b) and 1(c) are enlargement of area a and b in Fig. 1(a). According to Fig. 1(b), there are at least four phases readily identified from the brazed zone, including white (Ti,Zr)₂Ni matrix as marked by A, gray blocky Ti₂Cu and Ti₂Ni as marked by B and C, black blocky β -Ti as marked by D and E. The presence of these intermetallic phases will be proven by following TEM examination. Figure 1(c) displays the interface between the braze and Ti-15-3 substrate. There are fine precipitates in the Ti-15-3 grain, and it needs further TEM examination.

Figure 2 displays TEM micrographs and EDS chemical analysis results of the traditional furnace brazed Ti-15-3/Ti–20Zr–20Cu–20Ni/Ti-15-3 joint at 870°C for 1800 s. The brazed zone primarily comprised of (Ti,Zr)₂Ni matrix as illustrated in Fig. 2(a). According to Ni–Ti–Zr ternary alloy phase diagram, (Ti,Zr)₂Ni is a non stoichiometric com-

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Fig. 1. Microstructural observations and EPMA chemical analysis results of the traditional furnace brazed Ti-15-3/Ti-20Zr-20Cu-20Ni/Ti-15-3 joint at 870°C for 1800 s: (a) cross sectional overview of the joint, (b) higher magnification of area a in (a), (c) higher magnification of area b in (a).

Fig. 2. TEM micrographs and EDS chemical analysis results of the traditional furnace brazed Ti-15-3/Ti-20Zr-20Cu-20Ni/Ti-15-3 joint at 870°C for 1800 s: (a) BF image of central (Ti,Zr)₂Ni matrix, (b) BF image of the interface between (Ti,Zr)₂Ni matrix and β-Ti substrate, (c) BF image Ti₂Ni precipitate in β-Ti matrix, (d) DF image of Ti₂Ni precipitate using (022) spot with the zone axis of $[3\bar{1}1]$.

compound. It can be expressed as $(\text{Ti}_{1-x}\text{Zr}_x)_2\text{Ni}$ where x equals 0.21–0.30.¹⁷⁾ The structure type of $(\text{Ti,Zr})_2\text{Ni}$ is MgZn_2 . It has a hexagonal Laves structure with lattice constants of $a = 0.5191$ nm and $c = 0.8520$ nm. It is noted that $(\text{Ti,Zr})_2\text{Ni}$ is alloyed with Cu as marked by F and G in Fig. 2. The presence of $(\text{Ti,Zr})_2\text{Ni}$ intermetallic compound in Ti-20Zr-20Cu-20Ni brazed joint is very different from those in Ti-15Cu-15Ni and Ti-25Cu-15Ni brazed ones.^{10,18)} Brazed joints using Ti-Cu-Ni filler metals were mainly comprised of Ti₂Cu/Ti₂Ni intermetallic compounds, acicular α-Ti and retained β-Ti.¹⁰⁾ In contrast, $(\text{Ti,Zr})_2\text{Ni}$ intermetallic compound is the major phase in Ti-20Zr-20Cu-20Ni brazed joint, and $(\text{Ti,Zr})_2\text{Ni}$ is in contact with the β-Ti substrate as displayed in Fig. 2(b). Figure 2(c) displays the blocky Ti₂Ni and β-Ti. Based on Cu-Ni-Ti ternary alloy phase diagram, Ti₂Ni is alloyed with Cu up to 6–8 at%.¹⁷⁾ It is consistent with the EDS chemical analysis results. Ti₂Ni is alloyed with 7.6 at% Cu, 2.4 at% V and 5.7 at% Zr as marked by J,

Fig. 3. TEM micrographs and EDS chemical analysis results of the interface between the braze zone and Ti-15-3 substrate brazed at 870°C for 1800 s: (a) BF image of the β-Ti substrate close to the brazing interface, (b) DF image of $(\text{Ti,Zr})_2\text{Ni}$ compound along the β-Ti grain boundary using $(2\bar{1}11)$ spot with the zone axis of $[2\bar{1}\bar{6}]$ (c) BF image of the β-Ti substrate close to the brazing interface, (d) DF image of Ti₂Cu precipitate in the β-Ti grain using $(21\bar{1})$ spot with the zone axis of $[102]$.

and the β-Ti is primarily alloyed with β stabilizers, 3.1 at% Cu, 3.2 at% Ni and 10.1 at% V as marked by K in Fig. 2(c). All TEM analysis results are in accordance with the EPMA results as illustrated in Fig. 1(b).

Figure 3 shows TEM micrographs and EDS chemical analysis results of the interface between the filler metal and Ti-15-3 substrate brazed at 870°C for 1800 s. Based on Figs. 3(a) and 3(b), $(\text{Ti,Zr})_2\text{Ni}$ intermetallic compound is identified from the grain boundary between β-Ti grains. Meanwhile, Ti₂Cu precipitates are widely observed from inside grains of β-Ti as displayed in Figs. 3(c) and 3(d). Ti₂Cu is alloyed with 11.3 at% Ni and 3.4 at% Zr as marked by N in Fig. 3(c). It has been reported that that Ti₂Cu dissolves Ni up to 15 at%, and it is in accordance with the experimental observation.^{10,17,18)} It is obvious that the microstructure shown Fig. 1(c) consists of grain boundary $(\text{Ti,Zr})_2\text{Ni}$ and Ti₂Cu precipitates in the β-Ti matrix.

Solidification of Ti-20Zr-20Cu-20Ni melt results in forming primary $(\text{Ti,Zr})_2\text{Ni}$ and β-Ti. The β-Ti is transformed into Ti₂Cu, Ti₂Ni and retained β-Ti upon subsequent cooling cycle of brazing. For the interface between braze and Ti-15-3 substrate, the growth of $(\text{Ti,Zr})_2\text{Ni}$ intermetallic compound is primarily along the grain boundary of β-Ti substrate. The β-Ti substrate is alloyed with Cu, and Ti₂Cu precipitates are formed in β-Ti grain after brazing. Depletion of Cu, Ni and Zr from the braze melt into Ti-15-3 substrate during brazing results in forming grain boundary $(\text{Ti,Zr})_2\text{Ni}$ and Ti₂Cu precipitates in β-Ti grain. It is deduced that grain boundary diffusion of Ni and bulk diffusion of Cu in the β-Ti are related with the formation of grain boundary $(\text{Ti,Zr})_2\text{Ni}$ and interior Ti₂Cu precipitates in β-Ti grains. Because the Zr preferentially reacts with Ti and Ni to form grain boundary $(\text{Ti,Zr})_2\text{Ni}$, transport of Ni from the braze into Ti-15-3 substrate is enhanced via grain boundary diffusion of Ni. In contrast, there is no Ti₂Cu precipitate along β-Ti grain boundary. Grain boundary diffusion of Cu is not promoted in forming Ti₂Cu in β-Ti grain.

Figures 4(a)–4(c) display microstructural evolution of infrared brazed Ti-15-3/Ti-20Zr-20Cu-20Ni/Ti-15-3 joints at different brazing temperatures. Increasing the brazing temperature greatly enhances the depletion rate of Cu, Ni

Fig. 4. Microstructural evolution and EPMA chemical analysis results of infrared brazed Ti-15-3/Ti-20Zr-20Cu-20Ni/Ti-15-3 joints at (a) BEI, 850°C, (b) BEI, 890°C, (c) BEI, 910°C for 1800 s, (d) EPMA analyses across the brazed joint shown in (c).

Fig. 5. SEM micrographs of Ti-15-3 substrate: (a) original, (b) traditional furnace, (c) infrared furnace brazing at 870°C for 1800 s.

and Zr driven by concentration gradient from the braze melt into Ti-15-3 substrate during brazing. For specimens brazed at lower temperatures, most Cu, Ni and Zr are preserved in the brazed zone, and form $(\text{Ti,Zr})_2\text{Ni}$, Ti_2Ni and Ti_2Cu intermetallic compounds after brazing as illustrated in Figs. 4(a) and 4(b). For the specimens brazed at 910°C for 1800 s, Cu, Ni and Zr are depleted from the brazed zone due to concentration gradient as illustrated in Fig. 4(d). According to binary Cu-Ti and Ni-Ti phase diagrams, the maximum solubility of Cu and Ni in the β -Ti is 13.5 at% and 10 at%, respectively.¹⁹⁾ $(\text{Ti,Zr})_2\text{Ni}$, Ti_2Cu and Ti_2Ni intermetallic compounds are all disappeared from the brazed zone as displayed in Fig. 4(c). β -Ti dominates the entire joint for the specimen brazed at 910°C for 1800 s. It is expected that the disappearance of brittle intermetallic phases from the brazed joint is beneficial to bonding strength of the joint.

Figure 5 shows SEM micrographs of original Ti-15-3, traditional furnace and infrared furnace brazed Ti-15-3 substrates at 870°C for 1800 s, respectively. The coarsening effect of Ti-15-3 grains is not prominent in both infrared and traditional furnace brazed specimens. The original grain size of Ti-15-3 alloy is about 50 μm (Fig. 5(a)). Grain size of Ti-15-3 substrates is coarsened to approximately 100 μm in both specimens brazed at 870°C for 1800 s as illustrated in Figs. 5(b) and 5(c). Similar results are observed from traditional furnace and infrared brazed specimens due to the same brazing condition.

4. Conclusion

Microstructural observation of Ti-20Zr-20Cu-20Ni brazed Ti-15-3 alloy has been performed. For the specimen furnace brazed at 870°C for 1800 s, the joint is dominated by blocky Ti_2Cu , Ti_2Ni and β -Ti in $(\text{Ti,Zr})_2\text{Ni}$ matrix. Depletion of Cu, Ni and Zr from the braze melt into Ti-15-3 substrate during brazing results in forming grain boundary $(\text{Ti,Zr})_2\text{Ni}$ and Ti_2Cu precipitates in β -Ti substrate. The amounts of intermetallic phases in the brazed joint are greatly decreased with increasing the brazing temperature. For the specimen infrared brazed at 910°C for 1800 s, the joint is primarily comprised of β -Ti, and Ti_2Cu , Ti_2Ni as well as $(\text{Ti,Zr})_2\text{Ni}$ intermetallic phases are all dissolved into the Ti-15-3 substrate. Based on related binary alloy phase diagrams, the β -Ti can dissolve Cu, Ni and Zr. Most intermetallic compounds in the brazed joints are dissolved into the β -Ti matrix with appropriate brazing condition, and the β -Ti matrix dominates the entire brazed joint. The disappearance of brittle intermetallic compounds from the brazed joint makes the clad Ti-20Zr-20Cu-20Ni foil show great potential in brazing Ti-15-3 alloy for industrial applications.

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