Interfacial Reaction and Bonding Strength of Ti₅₀Ni₅₀ and Inconel 600 Dissimilar Brazed Joints

Ren-Kae Shiue¹, Shyi-Kaan Wu^{1,2,*}, Chun-Kai Liu² and Chuan-Yu Dai²

¹Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan

²Department of Mechanical Engineering, National Taiwan University, Taipei 106, Taiwan

The interfacial reaction and shear strength of Ti₅₀Ni₅₀ SMA and Inconel 600 alloy infrared brazed with a gold-based filler metal Au-22Ni-8Pd (BAu-6) were investigated. The shear strengths of Ti₅₀Ni₅₀/Au-22Ni-8Pd/Inconel 600 joints brazed for 180 s and 300 s were as high as 387 MPa and 527 MPa, respectively. Cracks initiated and propagated along the interface between Ti(Ni,Au)₃/TiNiAu eutectic and/or TiNi₂Au layer. The joints show high potential for industrial applications. [doi:10.2320/matertrans.M2017123]

(Received April 11, 2017; Accepted June 9, 2017; Published August 25, 2017)

Keywords: dissimilar brazing, Ti₅₀Ni₅₀, Inconel 600 alloy, gold-based filler, interfacial reaction, bonding strength

1. Introduction

Ti₅₀Ni₅₀ shape memory alloy (SMA) undergoes a thermo-elastic martensitic transformation and exhibits excellent shape memory effects, superelasticity, and damping capacity.^{1,2)} TiNi-based SMAs are well-known functional materials and can be used as shape-memory actuators. For example, Ti₅₀Ni₅₀ SMA actuators are used to replace exploding bolts utilized in nuclear power plants.³⁾ The actuator is made by brazing Ti₅₀Ni₅₀ SMA and the nickel-based alloy. Dissimilar brazing of Ti₅₀Ni₅₀ SMA and Ni-based alloy is a crucial issue in such an application.

Ni-Cr alloys have good corrosion and high-temperature resistance.⁴⁾ Inconel 600 alloy (Special Metals Corp., New Hartford, NY) is a typical Ni-Cr alloy and has a chemical composition of Ni-15.5Cr-8.0Fe-0.5Mn-0.2Si in wt pct, and it is widely applied in furnace muffles and heat exchangers.⁵⁾ Inconel 600 alloy is a stable Ni-rich solid solution, and its microstructure after solution heat treatment at 1,200°C and water quenching shows straight grain boundaries free of precipitates because the Cr is kept in solid solution.⁵⁾ Inconel 600 alloy was used in this study to investigate dissimilar brazing with Ti₅₀Ni₅₀ SMA because it has a desirable combination of high corrosion resistance and workability.

Ag-Cu eutectic, Ag-Cu-Ti and Ag-Ti fillers have been applied in brazing Ti₅₀Ni₅₀ SMA, and the brazed joints demonstrate acceptable joint strengths of above 100 MPa.^{6,7)} However, dissimilar brazing Ti₅₀Ni₅₀ SMA is seldom studied in literature.⁸⁾ Gold-based filler metals have been used to braze iron-, nickel- and cobalt-based alloys where oxidation and/or corrosion resistance is required. In our previous study,⁸⁾ Ti₅₀Ni₅₀ SMA was infrared brazed with 316L stainless steel (SS) using Au-22Ni-8Pd (in mass%, AWS classification: BAu-6) filler metal, and the joint infrared brazed at 1,050°C for 300 s achieved a shear strength of 204 MPa. Infrared brazing of Ti₅₀Ni₅₀ SMA and Inconel 600 alloy with Cu-sil-ABA (Ag-35.25Cu-1.75Ti in mass%) and Ticusil (Ag-26.7Cu-4.5Ti in mass%) filler metals has also been investigated. The joints infrared brazed with the former filler at 900°C for 300 s had a shear strength of 324 MPa, and those

brazed with the latter filler at 950°C for 180 s had a shear strength of 300 MPa.⁹⁾ Both Ni and Pd alloyed into the Au matrix significantly improve the corrosion and creep resistance of the braze alloy.¹⁰⁾ In addition, Au and Ni are completely miscible and form an FCC solid-solution at high temperature.¹¹⁾ Therefore, Au-22Ni-8Pd filler metal is considered to be a suitable filler for infrared brazing of Ti₅₀Ni₅₀ SMA and Inconel 600 alloy.

The purpose of this investigation is focused on dissimilar infrared brazing of Ti₅₀Ni₅₀ SMA and Inconel 600 alloy for industrial application. Wetting angle measurements, microstructures, shear strengths and failure analyses of infrared brazed joints are evaluated in the experiment.

2. Experimental Procedure

A Ti₅₀Ni₅₀ ingot of about 120 g was prepared in a vacuum arc remelter (VAR) from titanium and nickel (both 99.9 mass% in purity) pellets and remelted six times in ultra-high purity argon atmosphere with a pure titanium getter. The ingot was homogenized at 900°C for 3,600 s and then cut by a low-speed diamond saw to the specimen size. The specimens used in the experiment for wetting angle measurements and metallographical observations were templates with a dimension of 15 × 5 × 3 mm³, and those used for shear tests were templates of 15 × 7 × 4 mm³. Prior to brazing, the brazing surface was polished with SiC paper up to 1,200 grit and subsequently cleaned using an ultrasonic bath with acetone as the fluid. The Au-22Ni-8Pd foil, purchased from Wesgo Company (The Morgan Crucible Company, Berkshire, England), had a thickness of 50 μm with a liquidus temperature of 1,045°C.^{6,10)}

The dynamic wetting angle of Au-22Ni-8Pd filler metal on Ti₅₀Ni₅₀ and Inconel 600 substrates was evaluated in vacuum by sessile drop test using a filler ball of approximately 0.15 g. Schematic diagrams of the wetting angle measurement facility and the specimen holder during infrared brazing can be found in previous studies.^{12,13)} An infrared heating furnace (ULVAC SINKU-RIKO RHL-P816C, Tokyo, Japan) was used as the main body of the vacuum furnace. A vacuum of 5 × 10⁻³ Pa was maintained, and the heating rate was set at 15°C/s throughout the experiment. All specimens

*Corresponding author, E-mail: skw@ntu.edu.tw

were preheated at 700°C for 300 s, and they were infrared brazed at 1,050°C for 180 and 300 s.

Shear tests were performed to evaluate the bonding strengths of selected brazed joints. A symmetrical double lap joint, Inconel 600/Ti₅₀Ni₅₀/Inconel 600, was used for shear testing of the brazed joint, as in previous studies.^{12,14} Shear tests were conducted using a Shimadzu AG-10 universal testing machine (Shimadzu Corp., Nakagyo-ku, Kyoto, Japan) with a constant crosshead speed of 0.0167 mm/s. Cross-sections of infrared brazed joints were examined using a NOVA NANO 450 field-emission scanning electron microscope (FESEM) (FEI Corp., Oregon, USA) equipped with an energy-dispersive spectrometer (EDS). Its operation voltage was 15 kV and the minimum spot size was 1 μ m.

3. Results and Discussion

Figure 1 shows the results of dynamic wetting angle measurements of Au-22Ni-8Pd filler metal on Ti₅₀Ni₅₀ SMA and Inconel 600 alloy at 1,050°C for 300 s. The Au-22Ni-8Pd filler metal had very good wettability for both alloys. As shown in Fig. 1, the wetting angle of Ti₅₀Ni₅₀ SMA was

Fig. 1 Dynamic wetting angle measurements of Au-22Ni-8Pd filler metal on the Ti₅₀Ni₅₀ and Inconel 600 substrates tested at 1,050°C.

170° at the beginning, and it dropped quickly to 40° in the first 60 s before continuously and slowly decreasing to 27° at $\approx$ 100 s, where it remained steady up to 300 s. The presence of a two-step change in wetting angle measurement is resulted from interfacial reaction(s) between Au-22Ni-8Pd braze alloy and Ti₅₀Ni₅₀ SMA. The formation of interfacial reaction layer(s) leads to change in local chemical composition and melting temperature of the braze alloy. Additionally, the mass transport is retarded by the presence of reaction layer(s). Both reactive wetting and capillary flow of braze melt are slowed down.

For Inconel 600 alloy, the wetting angle was 130° at the beginning and decreased very slowly to $\approx$ 125° in the first 10 s, after which it continuously dropped to 20° at $\approx$ 90 s before remaining steady up to 300 s. It has been reported that the gold contained in Au-based filler metals can improve the wettability of many Ni-based substrates.^{15–18} According to the Au-Ni binary alloy phase diagram, Au is completely miscible with Ni at above 810.3°C.¹¹ Capillarity and the spreading behavior of the Au-based braze melt on Inconel 600 substrate are greatly enhanced by dissolution of Ni-based substrate into the Au-based braze melt.¹⁰ Comparing the curve of the dynamic wetting angle vs. the infrared brazing time of Au-22Ni-8Pd/Inconel 600 to that of Au-22Ni-8Pd/316L SS, the wetting of Au-22Ni-8Pd/Inconel 600 is much better than that of Au-22Ni-8Pd/316L SS.⁸ The dissolution of 316L SS substrate into the Au-based braze melt is inferior to that of Inconel 600 due to limited solubility of Fe in Au-based braze.¹¹

Figures 2(a) and 2(b) show the backscattered electron image (BEI) cross-sections of Ti₅₀Ni₅₀/Au-22Ni-8Pd/Inconel 600 joints and EDS chemical analysis results of joints infrared brazed at 1,050°C for 180 s and 300 s, respectively. Although interfacial reactions occur between Au-based braze alloy and Ti₅₀Ni₅₀ substrate, the figure shows a diffused interface free of any reaction layer between the braze and Inconel 600 substrate. The chemical composition of Au-22Ni-

Fig. 2 SEM BEI cross-sections and EDS chemical analysis results near the Ti₅₀Ni₅₀ substrate side (left) and the Inconel substrate side (right) of Ti₅₀Ni₅₀/Au-22Ni-8Pd/Inconel 600 joints infrared brazed at 1,050°C for (a) 180 s, (b) 300 s.

8Pd filler metal is 44.1 Au, 46.5 Ni, and 9.4 Pd in at%. The areas marked Aa and Ab are the $\text{Ti}_{50}\text{Ni}_{50}$ substrate near the interfacial layers, and their EDS results, shown in Fig. 2, indicate that they are Ni-rich TiNi SMA alloyed with Au solute. The infrared brazed joints are dominated by (Au,Ni) solid solution alloyed with Ti, Pd, Fe and Cr (marked Fa and Fb). The area on the $\text{Ti}_{50}\text{Ni}_{50}$ substrate side primarily consists of a layer of lamellar-like TiNi_3 intermetallic (marked Ba and Bb) in Ti-Ni-Au (I) intermetallic compound (marked Ca and Cb), and a layer of Ti-Ni-Au (II) intermetallic compound that is a discontinuous layer (marked Da) or a continuous layer (marked Db) next to the filler metal, as illustrated in Fig. 2. A few areas with lamellar eutectic (marked Ea) existed discontinuously in between layer D and the filler metal, with less of these areas in Fig. 2(b) than in Fig. 2(a). Also in Figs. 2(a) and 2(b), the area on the Inconel 600 substrate side consists of a layer of (Ni,Cr,Fe) solid solution (marked Ga and Gb) alloyed with Au, Pd and Ti solute atoms, but it has lower Ni, Cr, and Fe contents than those in Inconel 600 substrate (marked Ha and Hb).

From the EDS results in Fig. 2, one can find that the composition of Ti-Ni-Au (I) phase (marked C) is close to TiNi-Au but that of Ti-Ni-Au (II) phase is close to TiNi_2Au (marked D). Careful examination of the gray levels exhibited in Fig. 2 reveals that the Ba_1 and Bb_1 are darker than the Ba_2 and Bb_2 . This phenomenon can be explained by the EDS results in Fig. 2, in which Ba_1 and Bb_1 are identified as a TiNi_3 intermetallic with a few (Au + Pd) solute atoms, but Ba_2 and Bb_2 are a $\text{Ti}(\text{Ni,Au})_3$ intermetallic with more (Au + Pd) solute atoms than the former. In addition, as the brazing time increases, area Ba_2 decreases as compared to area Bb_2 , but area Cb_2 increases significantly as compared to area Ca_2 . This feature causes area Cb_2 to be an almost continuous layer separating areas Bb_1 and Bb_2 . At the same time, the thickness of layer D, in which a few small Bb_2 particles are embedded, increases with the longer brazing time. Area E shows a lamellar mixture of (Ni,Au) solid solution and $\text{Ti}(\text{Ni,Au})_3$ phase, which has also been observed in $\text{Ti}_{50}\text{Ni}_{50}/\text{Au-22Ni-8Pd}/316\text{L SS}$ joints infrared brazed at $1,050^\circ\text{C}$ for 180 s and 300 s.⁸⁾

The microstructural evolution and related reaction mechanisms on both substrate sides can be elucidated as follows. On the $\text{Ti}_{50}\text{Ni}_{50}$ substrate side, to identify the formed intermetallics observed in Fig. 2, related phase diagrams can be used to elucidate these phases. According to the Au-Ni binary alloy phase diagram, Au is completely miscible with Ni above 810.3°C .¹¹⁾ In contrast, Ti is highly reactive to Au and Ni, and the Ti-Au and Ti-Ni binary alloy phase diagrams contain many binary intermetallic compounds.¹¹⁾ Although a Ti-Ni-Au ternary alloy phase diagram would be useful in this case, but no such diagram is currently available. However, the phase diagram for Ti-Ni-Cu shows that TiNiCu and TiNi_2Cu intermetallics form in this ternary alloy system.^{8,19)} Comparing the Ni-Cu binary phase diagram with the Ni-Au one, one can find that both diagrams indicate complete solid solubility at high temperature.⁹⁾ In addition, the Ti-Cu and Ti-Au binary phase diagrams show that in the range of $\text{Ti} \leq 50$ at%, TiCu , TiCu_2 , and TiCu_4 intermetallics will form in the former, and TiAu , TiAu_2 , and TiAu_4 will form in the latter. The similarities exhibited in the above two binary phase

diagrams in the range of $\text{Ti} \leq 50$ at% suggest a high likelihood that TiNiAu and TiNi_2Au intermetallics would be indicated in a Ti-Ni-Au ternary alloy phase diagram.^{8,19)} Therefore, from the EDS chemical compositions indicated in Fig. 2, the layers Da and Db are identified as a TiNi_2Au intermetallic compound. The lamellae Ca and Cb in the layer (B + C) are TiNiAu compound, as discussed in the previous paragraph. The high brazing temperature of Au-22Ni-8Pd filler metal is can cause the molten braze to be over-saturated, which in turn thickens the reacted area C and layer D when the brazing time is increased, as shown in Figs. 2(a) and 2(b). Both C and D are alloyed with Pd. Au-22Ni-8Pd filler metal contains 46.5 Ni and 9.4 Pd in at%. The addition of Pd in the Au-based braze alloy can increase the antioxidation ability and enhance the wettability to base metals.^{8,20)} Thus, a better quality of joint between substrate and braze can be obtained.

For the Inconel 600 substrate side, the EDS chemical analysis results showed that the layers Ga and Gb had compositions in at% of around 70Ni-(10~16)Cr-(5~7)Fe alloyed with some Au and Pd solute atoms, which are proposed to be a stable FCC Ni-rich solid solution, similar to that of Inconel 600 alloy. No interfacial reaction compound formed at the interface of the Inconel 600 substrate side. Additionally, a diffused interface can be observed in Fig. 2.

Table 1 shows the average shear strengths of joints with two different brazing conditions. The shear strengths of $\text{Ti}_{50}\text{Ni}_{50}/\text{Au-22Ni-8Pd}/\text{Inconel 600}$ joints brazed at $1,050^\circ\text{C}$ for 180 s and 300 s were 387 MPa and 527 MPa, respectively. The unusual high shear strength of 527 MPa shown in Table 1 arose from the better formation of the fillet, shown in Fig. 3(b), which was caused by the excellent wetting and flow-out of the molten filler during brazing at $1,050^\circ\text{C}$ for 300 s. The size of the fillet in the brazed joint increased significantly as the brazing time increased, as illustrated in Figs. 3(a) and 3(b). According to Fig. 1, the wetting angles of the braze alloy on both substrates were below 30° , and stabilized after 120 s. The capillary flow of the molten braze

Table 1 Average shear strengths of infrared brazed joints.

substrate	brazing temperature	brazing time	average shear strength
$\text{Ti}_{50}\text{Ni}_{50}$, Inconel 600	$1,050^\circ\text{C}$	180 s	387 ± 12 MPa
$\text{Ti}_{50}\text{Ni}_{50}$, Inconel 600	$1,050^\circ\text{C}$	300 s	527 ± 28 MPa*

*with significant fillet outside the brazed joint

Fig. 3 The formation of the fillets outside specimens infrared brazed at $1,050^\circ\text{C}$ for (a) 180 s and (b) 300 s.

increased with increases in brazing time due to interfacial reaction(s) of Ti₅₀Ni₅₀ side and dissolution of Inconel 600 substrate into the braze melt. However, interfacial reaction(s) and dissolution of substrates resulted in chemical composition change of the braze melt. The change in chemical composition of local braze melt at both interfaces might result in increasing local liquidus/solidus temperatures of the braze melt, and the local braze melt was isothermally solidified during infrared brazing. The isothermally solidified structure should be avoided in brazing, because it resulted in forming solidification shrinkage voids in the joint.¹⁰⁾ According to the experimental observation, no solidification shrinkage void was observed from the joint. Therefore, both interfacial reaction between the braze alloy and Ti₅₀Ni₅₀ substrate and erosion of Inconel 600 substrate were confined during infrared brazing. High shear strengths of infrared brazed joints presented in Table 1 indicate that the Au-22Ni-8Pd filler metal is suitable for brazing Ti₅₀Ni₅₀ SMA and Inconel 600 alloy.

Figures 4(a) and 4(b) present SEM BEI cross-sections and an SEI fractograph of fractured Ti₅₀Ni₅₀/Au-22Ni-8Pd/Inconel 600 joints infrared brazed at 1,050°C for 180 s and 300 s, respectively. It can be seen clearly that the brazed joints in Figs. 4(a) and 4(b) all fractured along the lamellar Ti(Ni,Au)₃/TiNiAu eutectic (B + C) neighboring the TiN-

i₂Au (D) layer. Both SEM SEI fractographs shown in Fig. 4 demonstrate cleavage-dominated fracture. Additionally, the EDS chemical analysis results shown in Fig. 4 are also consistent with those of layers (B + C) and D in Fig. 2.

4. Conclusion

Au-22Ni-8Pd demonstrates good wettability on Ti₅₀Ni₅₀ and Inconel 600 substrates when brazed at 1,050°C for longer than 100 s. The infrared braze joints are dominated by a (Au,Ni)-rich solid solution. On the Ti₅₀Ni₅₀ side, the 180 s brazed joint is composed of a layer of TiNi₃ and TiNiAu eutectic lamellae and a layer of TiNi₂Au intermetallic. The layers in joints brazed for 300 s are rather similar to those in joints brazed for 180 s, but the area of TiNiAu and the thickness of the TiNi₂Au both increase. On the Inconel 600 side, in joints brazed for 180 s and 300 s, there was only a diffused layer of (Ni,Cr,Fe) solid solution alloyed with a few Au, Pd and Ti solute atoms next to the Inconel 600 substrate. The shear strengths of Ti₅₀Ni₅₀/Au-22Ni-8Pd/Inconel 600 joints brazed for 180 s and 300 s can reach 387 MPa and 527 MPa, respectively. The formation of the fillet from the flow-out of the (Au,Ni)-rich braze melt during infrared brazing increases the shear strength of the joint, especially that of the 300 s brazed specimen. Cracking initiated at the inter-

Fig. 4 SEM BEI cross-sections, SEI fractographs and EDS chemical analysis results of Ti₅₀Ni₅₀/Au-22Ni-8Pd/Inconel 600 joints infrared brazed at 1,050°C for (a) 180 s and (b) 300 s.

face of the $\text{Ti}(\text{Ni,Au})_3/\text{TiNiAu}$ eutectic and TiNiAu intermetallic layer in the joint brazed for 180 s, and at the interface of the TiNiAu and the TiNi_2Au layer in the joint brazed for 300 s. The use of Au-22Ni-8Pd filler in dissimilar brazing of $\text{Ti}_{50}\text{Ni}_{50}$ and Inconel 600 alloy shows great potential for industrial applications.

Acknowledgment

The authors gratefully acknowledge the financial support of this research provided by Ministry of Science and Technology (MOST), Taiwan, under grant number MOST 105-2221-E002-044-MY2.

REFERENCES

- 1) K. Otsuka and C. M. Wayman: *Shape Memory Materials*, (Cambridge University Press, London, 1998) pp. 1–96.
- 2) K. Otsuka and X. Ren: *Prog. Mater. Sci.* **50** (2005) 511–678.
- 3) L. McD. Schetky: *Trans. Mater. Res. Soc. Jpn.* **18B** (1994) 1131–1142.
- 4) W. F. Smith: *Structure and Properties of Engineering Alloys*, (McGraw-Hill, New York, 1993) pp. 498–520.
- 5) *ASM Handbook, Vol. 1, Properties and Selection: Irons, Steels and High-Performance Alloys*, 10th ed., (ASM International, Materials Park, 1990) pp. 951–952.
- 6) C. van der Eijk, Z.K. Sallom and O.M. Akselsen: *Scr. Mater.* **58** (2008) 779–781.
- 7) X.K. Zhao, J.W. Tang, L. Lan, J.H. Haung, H. Zhang and Y. Wang: *Mater. Sci. Technol.* **25** (2009) 1495–1497.
- 8) R.K. Shiue, S.K. Wu, C.P. Chen and S.H. Yang: *Gold Bull.* **48** (2015) 57–62.
- 9) R.K. Shiue, S.K. Wu and S.H. Yang: *Metall. Mater. Trans., A* **48A** (2017) 735–744.
- 10) M. Schwartz: *Brazing: for the Engineering Technologist*, (ASM International, Materials Park, 1993) pp. 109–111.
- 11) *ASM Handbook, Vol. 3, Alloy Phase Diagrams*, 10th ed., (ASM International, Materials Park, 1992).
- 12) R.K. Shiue, S.K. Wu and S.Y. Chen: *Acta Mater.* **51** (2003) 1991–2004.
- 13) R.H. Shiue and S.K. Wu: *Intermetallics* **14** (2006) 630–638.
- 14) R.K. Shiue, Y.H. Chen and S.K. Wu: *Metall. Mater. Trans., A* **44A** (2013) 4454–4460.
- 15) M. Schwartz: *Gold Bull.* **8** (1971) 2–8.
- 16) P. Siegmund, C. Guhl, E. Schmidt, A. Rossberg and M. Rettenmayr: *J. Mater. Sci.* **51** (2016) 3696–3700.
- 17) A. Laik, A.A. Shirzadi, R. Tewari, A. Kumar, T. Jayakumar and G.K. Dey: *Metall. Mater. Trans., A* **44A** (2013) 2212–2225.
- 18) Y. Liu, Z.R. Huang and X.J. Liu: *Ceram. Int.* **35** (2009) 3479–3484.
- 19) P. Villars, A. Prince and H. Okamoto: *Handbook of Ternary Alloy Phase Diagrams volume 8*, (ASM International, Materials Park, 1997) pp. 9846–9861.
- 20) G. Humpston and D.M. Jacobson: *Principle of Soldering and Brazing*, (ASM International, Materials Park, 2001) pp. 43–47.