Note

Microstructural Evolution of Brazing 304 Stainless Steel Using an Amorphous (Ni, Fe)-based Foil

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1. Introduction

304 stainless steel (304SS) belongs to the category of austenitic stainless steels, and it is featured with excellent formability, low price and good corrosion resistance.^{1,2)} Traditional fillers used in brazing 304SS are classified as Ag-, Cu- and Ni-based braze alloys.^{3–5)} Ag-based braze alloys have the advantage of low brazing temperatures. However, high cost and low corrosion resistance are major drawbacks of most Ag-based fillers. Cu-based braze alloys have the advantage of low material cost, but poor corrosion resistance prohibits them from certain industrial applications. Ni-based braze alloys are excellent alternatives in brazing stainless steels applied in moderate temperatures and corrosive environments.^{3–5)} Most Ni-based fillers are usually alloyed with Cr for improved corrosion resistance, and alloyed with B and/or Si for melting point depressants (MPDs).⁵⁾ The addition of B and/or Si into the Ni-based fillers may results in forming brittle intermetallic phase(s) in the joint.^{6,7)} Accordingly, the amount of B and/or Si addition(s) to the Ni-based braze alloy should be limited in order to obtain a robust joint.

Ni-based braze alloys have been suffered from high cost of Ni content in recent years. One of alternative approaches in reducing the cost of Ni-based filler is to replace partial Ni content by Fe in the braze alloy. VZ-2106 is a newly developed (Ni,Fe)-based amorphous brazing foil. The chemical composition of VZ-2106 in weight percent is 44Ni, 35Fe, 11Cr, 1.5Mo, 1.0Cu, 6.4Si and 1.5B. **Table 1** lists the chemical compositions of the commercial Ni-based fillers of BNi-2, BNi-3, and BNi-5.³⁾ Compared with traditional Ni-based braze alloys, lower Si or B contents of the braze alloy are beneficial to avoid forming brittle

intermetallic phase(s) in the joint after brazing. Additionally, lower Ni content of the braze significantly decreases the material cost of VZ-2106. Solidus and liquidus temperatures of VZ-2106 are 1 044°C and 1 154°C, which are comparable to most Ni-based braze alloys. Microstructural evolution of VZ-2106 brazed 304SS joint needs further study before applied in industry.

2. Experimental Procedure

Base metals used in the experiment were 304SS disks with the diameter of 15 mm and 3 mm in thickness. All joined surfaces were ground by SiC papers up to grit 1 000 and then ultrasonically cleaned by acetone prior to brazing. VZ-2106 foil with the thickness of 40 μm was chosen as the braze alloy. Vacuum brazing was performed under the vacuum of 5×10^{-3} Pa. The heating rate was set at 0.33°C/s throughout the experiment. All specimens were preheated at 1 000°C for 600 s prior to brazing in order to equilibrate temperature profile of the specimen. Specimens were brazed at 1 160°C, 1 175°C and 1 185°C for 600 s, 1 200 s and 3 600 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 μm . Tensile tests of selected brazed joints were performed based on the ASTM E8 specification, and a schematic diagram of the tensile test specimen was illustrated in **Fig. 1**. Failure analyses of fractured surfaces were conducted using the EPMA secondary electron images (SEIs).

3. Results and Discussion

Figure 2 shows EPMA BEIs (backscattered electron images) and WDS (wavelength dispersive spectroscopy) analysis results of 304SS/VZ-2106/304SS joint brazed at 1 175°C for 1 200 s. According to the figure, there is only Fe-rich matrix primarily alloyed with Ni, Cr and Si as marked by 3 in the brazement. High Ni content of the Fe-rich phase results in forming stable γ -Fe at room temperature. The microstructure of the braze joint using VZ-2106 filler foil is different from those using traditional Ni-based braze alloy.^{6,7)} Brazed joints using traditional Ni-based fillers, e.g., BNi-2 and BNi-3, were primarily comprised of borides and Ni-rich matrix. The presence of blocky borides was detrimental to bonding strength of the brazed joint.^{6,7)} Lower B content of the VZ-2106 braze alloy is attributed to the disappearance of boride from the brazement. Because the Fe-rich matrix is free of brittle boride, it is expected that a reliable joint can be obtained.

Interdiffusion between the VZ-2106 braze and 304SS substrate has little effect on the chemical composition of 304SS substrate close to the brazed joint as demonstrated by

Table 1. Chemical compositions of three commercial Ni-based braze alloys.³⁾

Braze Alloy	Chemical Composition (wt%)	Solidus Temperature (°C)	Liquidus Temperature (°C)
BNi-2	Ni–7Cr–3.1B–4.5Si–3Fe	990	1 000
BNi-3	Ni–3.1B–4.5Si–0.5Fe	980	1 035
BNi-5	Ni–19Cr–10.1Si	1 080	1 135

Fig. 1. The schematic diagram of the tensile test specimen.

Location	1	2	3
Ni	6.9	1.3	27.0
B	0.0	31.0	0.3
Cu	0.4	0.0	0.5
Fe	71.3	31.6	51.2
Mn	1.7	1.1	0.7
Cr	19.1	34.7	14.0
Si	0.6	0.1	6.1
Mo	0.0	0.1	0.3
phase	Close to 304SS	BCrFe	Fe-rich

Fig. 2. EPMA BEIs and WDS analysis results in at% of 304SS/VZ-2106/304SS joint brazed at 1 175°C for 1 200 s.

1 in Fig. 2. However, the grain boundary precipitation of B–Cr–Fe intermetallic compound is widely observed as marked by 2 in Fig. 2, and the stoichiometric ratio among B, Cr and Fe is close to one. **Figure 3** displays isothermal section of B–Cr–Fe ternary alloy phase diagram at 900°C.⁸⁾ According to the phase diagram, grain boundary precipitates illustrated in Fig. 2 are identified as BCrFe phase. The formation of grain boundary BCrFe precipitates consumes Cr content of 304SS substrate and/or VZ-2106 braze, so impairs their corrosion resistance. Additionally, the presence of grain boundary BCrFe precipitates may deteriorate interfacial strength of the brazed joint. It should be minimized via optimization of brazing conditions.

For traditional BNi-2 and BNi-3 braze alloys, the existence of B–Cr–Fe–(Ni) intermetallic compounds is observed along substrate grain boundary and the interface between braze alloy and stainless steel substrate.^{6,7)} Thick interfacial B–Cr–Fe–(Ni) layer was widely observed for all furnace/infrared brazed specimen.⁶⁾ Additionally, Kirkendall porosity was ever increased with increment of the brazing time and/or temperature. Kirkendall porosity and interfacial B–Cr–Fe–(Ni) layer cannot be removed by homogenization of the brazed joint.⁶⁾ In contrast, both Kirkendall porosity and interfacial reaction layer(s) are not found in the brazed joint using VZ-2106 filler foil due to its lower B content.

Figure 4 illustrates microstructural evolution of 304SS/VZ-2106/304SS joints under various brazing conditions. All brazing conditions result in sound joints, free of any void or

Fig. 3. Isothermal section of B–Cr–Fe ternary alloy phase diagram at 900°C.⁸⁾

crack. Based on aforementioned EPMA chemical analysis results, γ -Fe dominates entire brazed joints, and there is no second phase in the brazement. Microstructures of VZ-2106 brazed joints are insensitive to brazing temperature and time, and it is beneficial to be applied in industry. For example, the mass of industrial plate heat exchanger may exceed 500 kg. Huge temperature gradient is encountered in brazing the plate heat exchanger. A wider brazing process window significantly improves the yield of such a product. The VZ-2106 filler foil demonstrates good result in brazing 304SS.

According to Fig. 4, increasing the brazing temperature and/or time result in increasing the penetration depth of grain boundary BCrFe intermetallic compound. For the specimen brazed at 1 165°C for 600 s, most grain boundary BCrFe precipitates are localized close to the interface between the braze and 304SS as demonstrated in Fig. 4(a) with the penetration depth approximately 50 μ m. The penetration depth is increased above 100 μ m for the specimen brazed at 1 185°C for 3 600 s as displayed in Fig. 4(i). It is worth mentioned that grain boundary BCrFe precipitates are sparse in the 304SS substrate, especially for the specimen brazed at 1 185°C for 3 600 s. The microstructure of VZ-2106 brazed joint is significantly improved as compared with those of traditional Ni-based brazed specimens.^{6,7)}

Tensile test has been performed for 304SS/VZ-2106/304SS joint brazed at 1 185°C for 3 600 s. The brazed joint demonstrates average bonding strength of 433 MPa with the reduction area of 12%. Ductile dimple dominated fracture is widely observed from the fractured surface. Grain boundary BCrFe precipitates show little effect on tensile strength of the joint.

4. Conclusion

Microstructural evolution of VZ-2106 brazed 304SS has been evaluated. The brazed joint is dominated by γ -Fe alloyed with Ni, Cr and Si, and it is free of void and crack. Wide brazing process window and lack continuous brittle interfacial layer between the braze alloy and 304SS substrate make it superior to most traditional Ni-based braze alloys. VZ-2106 brazing foil shows great potential in brazing 304SS for industrial applications.

Fig. 4. EPMA BEIs of 304SS/VZ-2106/304SS joints brazed at (a) 1 165°C for 600 s, (b) 1 165°C for 1 200 s, (c) 1 165°C for 3 600 s, (d) 1 175°C for 600 s, (e) 1 175°C for 1 200 s, (f) 1 175°C for 3 600 s, (g) 1 185°C for 600 s, (h) 1 185°C for 1 200 s, (i) 1 185°C for 3 600 s.

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