Brazing of Mn–Cu Alloy and 430 Stainless Steel with Cu–34Mn–6Ni–10Sn Filler Metal

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In this paper, brazing of Mn–Cu damping alloy and 430 stainless steel (SS) using Cu–34Mn–6Ni–10Sn filler metal was carried out at different temperatures (850 °C to 880 °C) for different times (5 min to 12 min). The microstructure and mechanical properties of brazed joints were investigated. The results show that a (Fe, Mn) solid solution diffusion layer was formed at the interface between SS and brazing seam. The brazing seam was composed of a (Cu, Mn) solid solution phase and a (Cu, Mn, Sn) solid solution phase. Besides, the needle-like Mn–Cr–Cu–Fe compounds were found to distribute near the interface of each substrate and brazing seam. The grain boundary penetration of (Cu, Mn, Sn) solid solution phase led to the local melting of Mn–Cu alloy. The joint brazed at 870 °C for 10 min possessed the highest shear strength of about 212 MPa, the fracture occurred at the middle of brazing seam. [doi:10.2320/matertrans.M2019054]

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1. Introduction

Mn–Cu alloys have received much attention for their high damping capacity and mechanical properties,^{1,2)} and have been used for vibration and noise reduction in the fields of aerospace, automotive, nuclear industry and machinery manufacturing.^{3,4)} Ferritic stainless steels (SS) are widely used in industry for their good thermal conductivity, small expansion coefficient, good oxidation resistance, and excellent stress corrosion resistance.⁵⁾ Joining Mn–Cu alloys and ferritic stainless steels can achieve the material with complementary performance and expand the application of Mn–Cu alloy in engineering area. Considering the different chemical compositions and physical properties between Mn–Cu alloys and SS, brazing is a suitable choice to join these two dissimilar metals.^{6,7)}

Choosing the proper filler metal is one of the most important factors to obtain good brazed joint. Cu-based filler metals have good mechanical and wetting properties by adding alloying elements like Mn, Ag, Ni, Zn and Sn,^{8,9)} and have been widely used to join copper alloys and stainless steels. According to the binary phase diagrams, Mn and Ni can completely soluble in Cu.¹⁰⁾ The addition of Mn and Ni can improve the strength of Cu-based filler metals. However, the addition of Ni can increase the melting point of filler metals and result in the increase of brazing temperature. The intermetallic compounds formed at high brazing temperature will deteriorate the mechanical performance of joint.¹¹⁾ In a report,¹²⁾ the brazing of duplex stainless steels to Cr–Cu alloy with Cu–38Mn–9.5Ni filler metal (AWS4764) was carried out at 1000 °C. The broken pieces of stainless steel entered the liquid filler metal during brazing, the Mn–Fe phase, Mn–Cr phase and Cr–Fe phase were formed due to the dissolution of the base metals. Roy *et al.*¹³⁾ developed a 50Cu–40Mn–10Ni filler metal by melting spinning technique to lower the

melting point. The filler metal showed a narrow melting zone ($\Delta T = 45$ °C), with solidus and liquidus temperatures at 900 °C and 945 °C, respectively. The brazing of 304SS and pure copper was carried out at 920 °C, a little amount intermetallic compounds were formed in the joint. In fact, to join the Mn–Cu alloy and SS, the brazing temperature should be lower than the melting point of the Mn–Cu alloy (about 900 °C). Sn was confirmed to be able to reduce the melting point and improve the wettability of the filler metals.¹⁴⁾ Li *et al.*¹⁵⁾ found that Sn can decrease the melting points of Ag–Cu–Zn–Sn filler metals drastically. However, the excessive addition of Sn will increase the brittleness of filler metals owing to the formation of Cu₄₁Sn₁₁ and Ag₃Sn brittle compounds. Similarly, Chatterjee *et al.*¹⁶⁾ carried out the brazing of copper alloy and mild steel with Cu–10Mn–30Sn filler metal at only 750 °C. While the high amount of Sn caused the formation of Fe–Mn–Sn intermetallic compounds between the interface of mild steel and filler metal.

In this work, a Cu–34Mn–6Ni–10Sn filler metal was developed to join the Mn–Cu alloy and 430SS at the temperatures below 900 °C. The microstructure and melting characteristics of Cu–34Mn–6Ni–10Sn filler metal were studied. The microstructure and mechanical properties of Mn–Cu/SS brazed joints were investigated. And the effect of brazing temperature and time on the mechanical properties of brazed joints were also discussed.

2. Experimental Procedures

The Mn–Cu alloy and 430SS were used as the substrate materials, and their chemical compositions are listed in Tables 1 and 2, respectively. The Cu–34Mn–6Ni–10Sn filler metal was prepared by a vacuum induction furnace, then the

Table 1 Chemical composition of Mn–Cu alloy (mass%).

Cu	Mn	Al	Zn	Cr
48.10	46.55	1.55	3.00	0.80

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Table 2 Chemical composition of 430SS (mass%).

C	Si	Mn	P	S	Cr	Ni	Fe
0.11	0.74	1.00	0.043	0.028	17.00	0.05	Bal.

Table 3 Chemical composition of Cu–34Mn–6Ni–10Sn filler metal (mass%).

Cu	Mn	Ni	Sn
49.73	34.54	6.01	9.72

as-cast ingot was homogenized at 720 °C for 10 h followed by water quenching. The chemical composition of the filler metal is given in Table 3. To determine the liquidus temperature of the filler metal, differential scanning calorimetry (DSC, NETZSCH STA 449F3) analysis was carried out under argon atmosphere with a heating rate of 10 °C/min.

For brazing, both the Mn–Cu alloy and 430SS were cut into platelets of 30 mm × 30 mm × 3 mm, and the filler metal was cut into foils with the thickness of about 300 μm. The surface of substrate platelets and filler metal foils were polished using various grades of SiC papers and then ultrasonically cleaned in ethanol solution for 10 min. The typical sandwich brazed joint was used in the experiment, a filler metal foil was placed between Mn–Cu alloy and SS platelets, as shown in Fig. 1(a). To remove the oxides and prevent the further oxidation of samples, the brazing flux was smeared on the contact surfaces of filler metal and substrates. Finally, the assembled sample was put in the preheated furnace. Figure 1(b) shows the schematic diagram of the brazing thermal cycle. The brazing experiment was carried out at different temperatures (T) and times (t), the specific experimental parameters are presented in Table 4. The brazing sample was taken out from furnace until the temperature reduced to 770 °C. After cooling to room temperature, samples were cleaned in the citric acid solution.

The microstructure characterization of Cu–34Mn–6Ni–10Sn filler metal and Mn–Cu/SS brazed joints were analysed by a scanning electron microscope (SEM, FEI Quanta 250)

Table 4 Processing parameters in brazing experiments.

Brazing parameters	Brazing temperature ($T/^\circ\text{C}$)	Holding time (t/min)
	850, 860, 870, 880	10
	870	5, 7, 10, 12

equipped with an energy dispersive spectrometer (EDS). Additionally, the microhardness across the brazed joint was measured by a microhardness device (HXD-1000TM) using a load of 100 g. Shear tests were performed on a mechanical testing machine (CMT4304) with a travel speed of 0.5 mm·min⁻¹ at room temperature utilizing self-made clamp. The shear strength was calculated using the following equation: $\tau = F/A$, where F is the fracture load, and A is the contact area. The fracture surfaces were also observed by using SEM.

3. Results and Discussion

3.1 Filler metal analysis

Figure 2 shows the BSE image of the Cu–34Mn–6Ni–10Sn filler metal. It can be seen that there were two phases in the filler metal. The EDS analysis results listed in Table 5 shows that these two phases were (Cu, Mn, Ni) solid solution with different content of Sn. The Sn content of phase 2 was

Fig. 2 BSE image of Cu–34Mn–6Ni–10Sn filler metal.

Fig. 1 (a) Schematic of brazing sample, (b) Brazing thermal cycle.

Table 5 EDS analysis results of points marked in BSE image in Fig. 2 (mass%).

Points	Cu	Mn	Ni	Sn
1	52.15	34.45	6.10	7.30
2	45.54	33.57	6.12	14.77

about twice that of phase 1, which indicated that the segregation of Sn happened during the solidification process in filler metal casting. Due to the solution strengthening effect of Sn, the microhardness of the phase 1 and phase 2 reached 180.88 HV and 277.05 HV, respectively.

Since Sn can reduce the melting point, phase 2 contained higher Sn should have a lower melting point than phase 1, theoretically. However, the DSC thermogram of the Cu–34Mn–6Ni–10Sn filler metal has only one endothermic peak in the heating process, as shown in Fig. 3. The filler metal has a narrow melting zone, and the solidus and liquidus

Fig. 3 DSC thermogram of Cu–34Mn–6Ni–10Sn filler metal.

temperatures were 785 °C and 819 °C, respectively. Based on the results of the DSC study, the brazing experiments was determined to carry out at temperatures from 850 °C (about 30 °C above the liquidus temperature) onwards.

3.2 Microstructure of the Mn–Cu/SS brazed joints

Figure 4(a) depicts the BSE image of the microstructure of Mn–Cu/SS joint brazed at 870 °C for 10 min. The joint can be mainly divided into three regions: SS, brazing seam and Mn–Cu alloy. The brazing seam was composed of a grey matrix phase and a white phase distributed at the grain boundary of matrix phase. And there were needle-like compounds distributed near the interfaces of both SS/brazing seam and Mn–Cu/brazing seam (the blue arrows pointed areas in Fig. 4(a)).

The microstructure of SS/brazing seam interface region is presented in Fig. 4(b), and the EDS analysis results of points in Fig. 4(b) are listed in Table 6. The results show that a (Fe, Mn) solid solution diffusion layer with small amounts of Cu, Cr and Ni (point 1) was formed between SS and brazing seam. According to Fe–Mn and Fe–Cu phase diagrams, Mn is completely soluble in Fe and the solubility of Cu in Fe is low. Therefore, the diffusion distance of Mn in SS was longer than that of Cu.¹³⁾ The formation of solid solution diffusion layer indicated that the bonding between SS and brazing seam was strong. However, the mismatch of linear expansion coefficient between SS and brazing seam led to the high residual stress at the interface region. As a result, the microcracks were formed at the interface.^{17,18)} In brazing seam, the grey matrix phase (point 2, 4 and 5) was (Cu, Mn) solid solution with varying content of Sn, Ni, Fe and Cr. And the white phase (point 3) was (Cu, Mn, Sn) solid solution which contained higher Sn and lower Mn compared to the matrix phase. The high content of Sn in white phase was also directly confirmed by the distribution feature of Sn element in Fig. 4(c). The white phase has a lower melting point and solidified at the grain boundary of matrix phase during cooling process. What's more, the matrix phase, which

Fig. 4 BSE images of the microstructure of (a) Mn–Cu/SS joint brazed at 870 °C for 10 min and (b) the interface region of SS/brazing seam, surface scan of Sn (c) and Cr (d) of (b).

Table 6 EDS analysis results of points marked in SS/brazing seam interface region in Fig. 4(b) (mass%).

Points	Fe	Cr	Mn	Cu	Ni	Sn	Al	Si	Zn
1	25.30	4.63	62.26	5.92	1.14	0.07	0.41	0.12	0.15
2	0.85	0.28	48.06	45.67	2.06	1.41	0.61	0.00	1.05
3	0.32	0.04	32.53	50.40	1.46	13.37	0.55	0.00	1.33
4	1.07	0.29	47.56	45.50	2.30	1.85	0.58	0.00	0.86
5	1.34	0.47	49.99	42.83	2.31	1.57	0.65	0.02	0.82

Fig. 5 BSE image of the needle-like compounds in the brazing seam of Mn–Cu/SS joint.

contained a small amount of Sn, was distributed adjacent to the SS, therefore, no intermetallic compounds of Sn were formed at the interface of SS/brazing seam. According to the distribution feature of Cr element, as shown in Fig. 4(d), the needle-like compounds distributed near the interface of SS/brazing seam were rich in Cr. Since there was no Cr in the designed filler metal, the formation of these needle-like compounds should be attributed to the dissolution of SS substrate.

Figure 5 shows the microstructure of needle-like compounds distributed in brazing seam. It can be seen that the interface between the compounds and the phases in brazing seam was sharp. The EDS results showed that the compound (marked by red point in Fig. 5) contained 62.74 mass% Mn, 16.98 mass% Cr, 10.69 mass% Cu and 5.37 mass% Fe with little amount of Sn, Ni and Zn. Therefore, it should be the compound of Mn–Cr–Cu–Fe. During the brazing process, the elements of SS such as Fe and Cr dissolved into the liquid filler metal, and resulted in the formation of the needle-like Mn–Cr–Cu–Fe compounds. The solidification of liquid filler metal usually started from the interface regions of substrates and filler metal, therefore, the compounds mostly distributed near the interface regions in brazing seam.

At the Mn–Cu alloy side, the (Cu, Mn, Sn) solid solution phase penetrated in the grain boundaries of Mn–Cu alloy, which caused local melting of Mn–Cu alloy. The melted alloy entered the liquid filler metal. As a result, the Mn content of (Cu, Mn) solid solution matrix phase in brazing seam was

Fig. 6 The microhardness of Mn–Cu/SS joint brazed at 870 °C for 10 min.

higher than that of the designed filler metal, and the width of brazing seam was increased. Due to the similar element compositions of Mn–Cu alloy and filler metal, the epitaxial solidification was observed between brazing seam and Mn–Cu alloy. There was no clear boundary between brazing seam and Mn–Cu alloy.

Microhardness profile is a good indicator of the joint's microstructure. Figure 6 shows the microhardness distribution feature of Mn–Cu/SS joint brazed at 870 °C for 10 min. Their average hardness was 152 HV and 140 HV for SS and Mn–Cu alloy, respectively. Due to the solution strengthening of Mn and Sn, the hardness of brazing seam was close to that of SS substrate. But the middle region of brazing seam has relatively low hardness. What's more, the regions where needle-like Mn–Cr–Cu–Fe compounds distributed (marked by the dotted lines in Fig. 6) showed the highest hardness value of about 184 HV. The size of needle-like Mn–Cr–Cu–Fe compounds was much smaller than the size of indentation, it might be the high hardness of compounds resulted in the high hardness of their distributed regions.

3.3 Shear strength of brazed joints

Figure 7 shows the shear strength of Mn–Cu/SS joints brazed at different brazing temperatures for different times. In Fig. 7(a), as the brazing temperature increased from 850 °C to 870 °C, the shear strength of brazed joints increased from 173 MPa to 212 MPa. However, the shear strength of joints

Fig. 7 Shear strength of joints brazed at different brazing temperatures (a) for different holding times (b).

Fig. 8 BSE images of the fractured joint.

Fig. 9 Fracture surfaces of the brazed joint, (a) 430SS side, (b) Mn-Cu alloy side.

reduced to 200 MPa as the brazing temperature increased to 880 °C. In Fig. 7(b), the shear strength of brazed joints increased gradually as the time increased from 5 min to 10 min at 870 °C, but the strength value decreased as the holding time extended to 10 min. Figure 8 shows the fractural position of joint brazed at 870 °C for 10 min. It can be seen that the fracture mainly occurred at the middle of brazing seam. The slip bands and dimples were observed in the fracture surfaces in Fig. 9, which demonstrated that the joint exhibited the ductile fracture characteristic. The EDS analysis results show that the (Cu,Mn) matrix phase at the middle of brazing seam has lower Mn content. This illustrated that the microstructure of brazing seam was inhomogeneous. The microhardness results in Fig. 6 also indicated that the middle

region of brazing seam was weaker in the joint. Therefore, the joint fractured at the middle region of brazing seam during shear test.

Figure 10 presents the microstructures of Mn-Cu/SS joints brazed at different temperatures. With the increase of brazing temperature, the brazing seam became wider due to the increased melting quantity of Mn-Cu alloy. The widening of brazing seam aggravated the inhomogeneity of microstructure. When the brazing temperature lower than 870 °C, although the brazing seam was widening, element Mn dissolved from the melted Mn-Cu alloy strengthened the brazing seam. Therefore, the shear strength of brazed joints was increased gradually. However, at higher temperature, the excessive melting of Mn-Cu alloy not only led to the further

Fig. 10 BSE images of Mn–Cu/SS joints brazed at different temperatures, (a) 850 °C, (b) 860 °C, (c) 870 °C, (d) 880 °C.

widening of brazing seam but also caused the coarsen of grains in the brazing seam. As a result, the strength of brazing seam decreased accordingly.¹⁹⁾ The effect of holding time on the shear strength of brazed joints was similar with that of brazing temperature.

4. Conclusions

In this work, the brazing of Mn–Cu damping alloy and 430SS using a Cu–34Mn–6Ni–10Sn filler metal was carried out. The following conclusions can be drawn.

- (1) The Cu–34Mn–6Ni–10Sn filler metal was composed of two (Cu, Mn) solid solution with different Sn content, and the melting point of the filler metal was 819 °C.
- (2) A (Fe, Mn) solid solution diffusion layer was formed at the interface of SS/brazing seam. The brazing seam was composed of a (Cu, Mn) matrix solid solution phase and a (Cu, Mn, Sn) solid solution phase. Besides, some needle-like Mn–Cr–Cu–Fe compounds were formed near the interface of each substrate and brazing seam. The melting of Mn–Cu alloy has great effect on the microstructure of brazing seam.
- (3) With the increase of brazing temperature and holding time, the shear strength of Mn–Cu/SS brazed joint increased at first and then decreased. The joint brazed at

870 °C for 10 min showed the highest shear strength of about 212 MPa. The joint fractured at the middle of brazing seam, and the fracture showed ductile fracture characteristic.

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