Mechanical Properties and Microstructure of Pure Copper Joints Brazed with Amorphous Cu68.5Ni15.7Sn9.3P6.5 Filler Metal

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Abstract — Pure Cu is brazed with amorphous Cu68.5Ni15.7Sn9.3P6.5 (wt.%) filler metal in a vacuum furnace. The effects of dwelling time and brazing temperature on the tensile strength and microstructure of the brazed joints are investigated. The bonding mechanism of the joints is also discussed. It is found that the tensile strength firstly increased and then decreased with increasing dwelling time or brazing temperature. The brazed joints contain Cu13.7Sn86.7, Cu3P and (CuNi)2P phase. The content of brittle Cu3P governs the tensile strength of the joints. The maximum tensile strength of the brazing joints is found to be 135 MPa when brazing was performed at 680°C for 20 min. In addition, the bonding mechanism of the joints shows the characteristics of contact reaction brazing before the temperature reaches the melting point. The fractured surface is characterized by brittle fracture.

Keywords — Cu-P amorphous filler metal; vacuum brazing; microstructure; bonding mechanism

I. INTRODUCTION

Traditional Cu-P filler metals have been widely used for brazing of Cu and its alloys due to their low melting point, superior wettability, perfect self-fluxing and low cost. However, when more than 5 wt.% P is used, a brittle intermetallic compound (IMC), Cu3P tends to form at room temperature. Therefore, the processing of traditional Cu-P filler metals gets very difficult [1]. Thus, it is necessary to discover new kinds of Cu-P filler metals. In recent years, some amorphous Cu-Ni-Sn-P filler metals such as MBF2005P alloy ribbons have been manufactured using rapid solidification [2, 3]. A number of advantages such as extremely high chemical and phase homogeneity, higher diffusivity and narrow melting and solidification ranges have been reported for these amorphous alloys. Their flexibility and ductility are superior to the traditional Cu-P filler metals [4]. The Cu-Ni-Sn-P amorphous filler metals can be made into various shapes and are widely used. However, the number of studies on the Cu-Ni-Sn-P amorphous brazing joints is scarce [5, 6]. Thus this study attempts to investigate the influences of brazing temperature and time on the interfacial microstructure, phase constitution and tensile strength of the Cu-Ni-Sn-P amorphous brazing joints. The bonding mechanism of the brazing joints is also analyzed.

II. MATERIALS AND EXPERIMENTAL METHODS

Pure Cu (≥99.9%, wt.%) were used as the base metals in this experiment. The base metals were cut into workpieces with the dimensions of 25mm×25mm×2mm and Φ16mm×40mm for microstructure analysis and tensile test, respectively. The nominal chemical composition of Cu-Ni-Sn-P filler metals were 15.7% Ni, 9.3% Sn, 6.5% P and 68.5% Cu. The amorphous filler foils with 30 mm thick and 20 mm wide were prepared by melt spinning. Prior to brazing, the surfaces to be brazed were polished using SiC papers up to 1000 grit and ultrasonically cleaned in acetone for 15 min. The Cu/amorphous Cu68.5Ni15.7Sn9.3P6.5/Cu sandwich was assembled and then put into a special clamp. A vacuum furnace was employed to braze the samples. Following parameters were chosen during the vacuum brazing: vacuum level of 1×10⁻² Pa, dwelling time, t=5~30 min, the heating rate of 15 °C/min. All the specimens were furnace-cooled to room temperature after brazing. According to the differential thermal analysis (DTA) which was measured at a heating rate of 10 K/min, the solidus and liquidus temperature of the amorphous foil is 597 °C and 630.9 °C, respectively. Hence the brazing temperature was selected in the range of 660~720 °C. The time-temperature profile of the brazing cycle is shown in Figure1. After brazing, the joints were cut using a low-speed wire cutter; the cross sections of the joints were polished with 1000# metallographic sandpaper followed by polishing with 0.5 mm diamond paste. The microstructure and phase composition of joints interfacial were examined using scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. The elemental distribution in the brazed joints and the fracture surface was examined by using a electron probe microanalyzer (EPMA). Room temperature tensile tests were performed using the universal testing machine at a displacement rate of 1 mm/min to determine the mechanical strength of the joints. For each set of experimental data, minimum three samples were tested to average the joint strength.

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III. RESULTS AND ANALYSIS

A. Structure of Cu68.5Ni15.7Sn9.3P6.5 Amorphous Foil

Figure 2 shows a typical X-ray diffraction (XRD) pattern taken from Cu68.5Ni15.7Sn9.3P6.5 amorphous filler foil. Unless a spacious diffraction peak at ~40° there is no obvious diffraction peak corresponding to any crystallization can be observed. After polishing the surface, XRD pattern of the sample found to be identical as the former, indicating the whole sample remains amorphous.

B. Microstructure of the Brazed Joints

The microstructure of the joints brazed with Cu68.5Ni15.7Sn9.3P6.5 foil at 680°C for 20 min is shown in Figure 3. It is clearly seen that sound metallurgical bonding between the filler metals and Cu substrates. No micro-pore or crack exists in the brazed seams. The interface of the joints displays dark residual filler metals layer and light grey diffusion-reaction layer, which can be subdivided into three phases marked as A, B and C in Figure 3. In order to further investigate the interfacial microstructure, major elements at each spot in Figure 3 detected by EDS are listed in Table 1. X-ray diffraction analysis was carried out on the fracture interface of joints shown in Figure 4.

Based on the EDS results, phase diagram and Figure 4, the block grey phase marked as A is enriched with P (~22.82 at.%), Cu (~76.83 at.%) and a small quantity of Sn. The less dark grey phase marked as B is enriched with P (~21.52 at.%), Ni (~46.76 at.%) and Cu (~76.83 at.%). The light grey phase marked as C is enriched with Cu (~92.64 at.%). It can be identified that A is hexagonal phase Cu3P, B is an IMC having the chemical formula of (CuNi)2P, C adjacent to the Cu substrates is solid solution fcc - Cu13.7Sn86.3. Brittle IMCs such as Cu3P and (CuNi)2P are produced during crystallization with increasing the brazing temperature [7], and they will certainly degrade the mechanical properties of the joints.

Figure 5 shows the elemental maps of the joints brazed at 680°C for 15 min by means of EPMA. It can be seen from Figure 5(c-e) that though certain amount of Ni diffuses into the Cu substrate, a large quantity of Sn still distributes in the residual filler metal layer, and all the Sn diffuses from filler metals into the diffusion-reaction layer. However, no P diffuses into the Cu substrate and still exists in the residual filler metal layer.
Figure 5  (a) EPMA map scanning results of the joint brazed at 680 °C for 15 min; Elemental distribution map of (b) Ni, (c) Sn, (d) P, (e) Cu.

Figure 6  Interfacial microstructures of the joints brazed at different temperature for 10 min (a) 660 °C (b) 680 °C (c) 690 °C.

Figure 6 shows the microstructure of the joints brazed at different temperatures for 10 min. Microstructure of the joints obviously changes with increasing the brazing temperature. When the joints are brazed at 660 °C, the thickness of the residual filler metals layer is found to be almost identical to that of the initial filler metals, as shown in Figure 6(a). This phenomenon indicates that the interdiffusion and interaction between the filler metals and Cu substrates become slow or negligible because of the lower brazing temperature. When the joints are brazed at 680 °C, a large amount of continuous grey phase (Cu3P) and less scattered dark grey phase ((CuNi)2P) are formed between the Cu substrates (Figure 6(b)). The content of Cu3P phase evidently decreases when the brazing temperature rises up to 690 °C (Figure 6(c)). Only a small amount of discontinuous grey phase Cu3P exists in the brazing joints. With increasing the brazing temperature, the white diffusion-reaction layer becomes thicker and oppositely, the dark residual filler metal layer becomes thinner.

Figure 7. Interfacial microstructures of the joints brazed at 680 °C for different brazing time (a) 5 min (b) 10 min (c) 15 min

Figure 7 exhibits the microstructure of the joint brazed at 680 °C for different dwelling time. It can be observed from Figure 7 that the thickness of the residual filler metals layer decreases with increasing brazing time. However, the dwelling time does not affect the formation of the irregular interface.

C. Tensile Strength of the Joints

The effect of different brazing time on joint strength brazed at 680 °C is shown in Figure 8. It is evident that the tensile strength increases up to 20 min from 5 min and then declines from 20 min to 30 min. The tensile strength reaches the maximum of 135.19 MPa for 20 min. Short brazing time (5 min) leads to insufficient atomic diffusion between the melting filler metal and the Cu substrate, and thus the tensile strength appears to be lower (only 80.5 MPa). With the prolonging of brazing time, the thickness of the reaction layer also increases. Nevertheless, further prolonging the brazing time reduces the bonding strength because of grain growth. It can be seen that too short or too long brazing time could not produce strong joint; whereas a medium brazing time is capable to make a joint with higher strength.

Figure 8  Effect of different brazing time at 680 °C on tensile strength of the joints.
Figure 9 shows the effect of different brazing temperature on the tensile strength of the joints brazed for 10 min. It is clearly seen that the effect of brazing temperature on joint strength is similar to that of brazing time. Increasing the brazing temperature or prolonging dwelling time can improve dissolution and diffusion between filler metals and base metals, enhance metallurgical reaction and reduce the amount of IMCs Cu3P and (CuNi)2P. It causes drop in mechanical strength. However, when the brazing temperature is too high or the dwelling time is too long, the joint strength reduced sharply.

Figure 9  Effect of different brazing temperature for 10 min on tensile strength of the joints

Figure 10 shows the fractured surface of specimens brazed at 680 °C for 20 min after tensile test. It can be clearly seen that there are some wormlike pores on the fractured surface due to the vaporization of P in Cu3P. Therefore it can be assumed that more pores will be formed with increasing the temperature. The pores decrease the density of brazing joints. Figure 11 shows the fractograph of the specimen brazed at 680 °C for 20 min after room temperature tensile test. This can be characterized by brittle fracture. Based on the XRD analysis shown in Figure 4, the brittle nature is attributed to the existence of brittle IMCs Cu3P and (CuNi)2P.

Figure 10  Image of the fractured surface of specimens brazed at 680 °C for 20 min after tensile test.

Figure 11  Fractograph of the fractured surface of specimens brazed at 680 °C for 20 min after tensile test.

D. Brazing Mechanism of the Joints

The solidus temperature of the filler metal is found to be 597°C in this experiment. However, it can be seen that the interface of the filler metals partially contacted with the Cu substrates melts, and the filler metals are tightly bonded with Cu substrate (Figure 12) when the brazing was performed at 580 °C for 15. However the filler metals in quartz tube remains unchanged. This phenomenon indicates that there is contact reaction between the base metals and filler metals before reaching the melting point. Sn, as an active and melting point depressant element, diffuses out of the filler metals to base metals by solid diffusion, and reacts with Cu to form liquid phase, Cu6Sn5 at the interface of Cu/filler alloy. The liquid phase, Cu6Sn5 prefers to diffuse along the grain boundaries in depth direction. Hence, a network of liquid phase inside the brazing seam is formed. Obviously, the distribution of liquid phase may speed up the material exchange and continuous flow between liquid phases. With increasing either brazing temperature or brazing time, the filler metals melt and the liquid filler metals begin to spread and flow. The solid base metals react and continuously melt into filler metals until reaching the maximum saturated concentration, so the dissolution stops. Simultaneously, elemental P and Ni speed up the diffusion towards the base metal through liquid phase channel, which contribute to the formation of Cu-solid solution containing elements Sn, P, Ni [8-10]. Thus the content of IMCs Cu3P and Ni2P in the residual filler metals gradually reduces.

IV. CONCLUSIONS

(1) Perfect brazing joints of pure Cu can be obtained using the amorphous Cu-Ni-Sn-P filler foils. The brazing joints consist of dark residual filler metals layer and the light grey diffusion-reaction layer, which contain three phases: Cu (Cu13.7Sn86.3), Cu3P and (CuNi)2P.

(2) Interfacial morphology of the joints is greatly affected by the brazing temperature and brazing time. The content of IMCs, Cu3P and (CuNi)2P in the brazing residual layer decreases with increasing the brazing temperature and brazing time.

(3) Joint strength first increases and then decreases with increasing brazing temperature or dwelling time.

(4) Fractured surface is characterized by brittle fracture.

(5) The bonding mechanism of the joints has the characteristics of contact reaction brazing. The solidus Cu substrates react with element Sn and form liquid phase Cu6Sn5 at the interface of Cu/filler alloy.
REFERENCES