Research Article

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Micromorphology change and microstructure of Cu-P based amorphous filler during heating process

<https://doi.org/10.1515/htmp-2019-0013>

Received May 21, 2018; accepted Nov 08, 2018

Abstract: The changes that occur in the microstructure of crystalline and amorphous Cu-P-Sn-Ni filler metals during the heating process were studied by high-temperature microscopy, and the composition of solders at certain temperatures were analyzed by scanning electron microscopy and X-ray diffraction. The amorphous solder was observed to transform from amorphous to crystalline during the process of heating and distinct surface morphology changes were apparent, while the internal structure of the crystalline brazing filler metal was found to be relatively stable. During the heating process, the amorphous brazing filler metal formed a γ -Cu solid solution with a small amount of Cu_3P compounds, $\text{Cu}_{88}\text{Sn}_{22}$ and $(\text{Cu}, \text{Ni})_3\text{P}$ phase compounds, ultimately forming the $\text{Cu}_{88}\text{Sn}_{22} + \text{Ni}_{12}\text{P}_5 + (\text{Cu}, \text{Ni})_3\text{P}_3$ three-element eutectic structure.

Keywords: Cu-P based filler, Amorphous filler metal, Microstructure, Phase analysis, Brazing

1 Introduction

The amorphous Cu-P-based filler metal is an amorphous material obtained by rapid cooling when the filler metal is in a liquid state. In the process of rapid cooling, crystallization of the filler metal can be induced when the material deviates from an equilibrium state. However, the amorphous Cu-P-based filler metal will preserve its atomic structure exhibited while in the liquid state, and these properties will imbue the amorphous filler metal with high toughness,

high strength, and good electrical and thermal conductivity [1–4].

Compared with the crystalline filler metal, a brazed joint comprising amorphous filler metal exhibits a finer structure and a uniform inclusion distribution in the composition, which can reduce the soldering gap of the brazed joint and significantly improve the quality [5–7]. The microstructure and composition of brazing joints primarily depend on the structure and composition of the filler metal. During the heating process, the amorphous filler metal can transform from amorphous to crystalline. When a crystalline solder reaches its melting point, it wets and spreads on the base metal material until it finally cools and solidifies to complete the brazing process [8–10]. Domestic and foreign scholars have posited that amorphous and crystalline brazing filler metals both exhibit the same brazing mechanism. However, during the crystallization process of the amorphous filler metal as it nucleates and grows in the solid phase, the grain growth of the amorphous filler metal is mainly composed of equiaxed grains while that of the crystalline filler is mainly dendrites; and these dissimilar grain growth processes would also affect the properties of the brazed joints [11–14]. Decristofaro *et al.* have reported early studies of amorphous Ni-based solders indicating that joints brazed with amorphous brazing materials have superior properties. Further, they report that the wettability has the advantage that the amorphous brazing material does not contain flux and thus contamination is not introduced by the brazing agent during brazing. Studying amorphous brazing solders, Rabinkin *et al.* of U.S. United Signal Corporation have found that little eutectic exists in the central area of the brazed joint of an amorphous brazing filler metal, and only a small amount of discontinuous chromium-boron compound exists at the interface with the base metal. Therefore, the strength of the brazed joint is high [15–17].

In this paper, the characteristics and interface structure wetting mechanism of an amorphous filler metal are compared with a crystalline filler metal during the heat-

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Figure 1: Surface morphology evolution during heating of the crystalline brazing filler metal at (a) 180, (b) 450, (c) 500 and (d) 600 °C

Table 1: Chemical composition of filler metal

Materials	Chemical compositions (%)			
	Cu	P	Sn	Ni
amorphous filler metal	78.64	7.35	8.27	5.74
crystalline filler metal	76.82	7.57	8.99	6.63

ing process, and the differences and relations between the amorphous and crystalline filler metals are discussed.

2 Experimental details

The Cu-P-Sn-Ni amorphous brazing filler metal and crystalline brazing filler metal possessing the same composition were used as the brazing filler metals herein, where the chemical composition is shown in Table 1. The brazing filler metal was prepared in the form of a foil with a thickness of 0.08 mm and cut into a rectangular shaped samples with dimensions 20 mm × 5 mm.

The crystallization temperature of the filler metal was measured by a combined thermo-gravimetric analyzer, differential thermal analyzer and differential scanning calorimetric (DSC) analyzer (Pyris Diamond, Perkin Elmer Inc.). The surface of the brazing filler metal was ground by metallographic sand paper (1200#) followed by diamond grinding paste (5#, 3#, 1.5#) until the metal surface was polished smooth. Subsequently, the brazing filler metal was cut into 5×5 mm² pieces and placed in the chamber of a high-temperature metallographic optical microscope (Axio Imager A2m, Carl Zeiss Microscopy LLC) that was evacuated to 1.0×10^{-1} Pa, whose heating rate was 80 °C/min. The brazing filler metal was then heated to various temperatures and observed using the high-temperature microscope, while the micromorphology of the filler metal surface etched by a FeCl₃, HCl and H₂O (1 ml:50 ml:100 ml) mixed solution was observed under the metallographic microscope. The elemental composition of the samples was evaluated by scanning electron microscopy (SEM; JEOL-6480), while the elemental distribution and the phase constituents present on the interface were respectively examined using energy-dispersive

Table 2: Melting temperature of the brazing filler metal

	Crystallization temperature/°C	solidus temperature/°C	liquidus temperature/°C	Solid-liquid interval/°C
Amorphous filler metal	207	601.0	623.4	22.4
Crystalline filler metal	-	604.8	628.6	23.8

Figure 2: Surface morphology evolution during heating of the amorphous brazing filler metal during heating process at (a) 20, (b) 450, (c) 500, (d) 550 and (e) 600°C

Figure 3: Cu-P-Sn ternary phase diagram (10% Sn). “F” indicates $\text{Cu}_{13.7}\text{Sn}$ (face-centered cubic); “B” indicates $\text{Cu}_{5.6}\text{Sn}$ (body-centered cubic); “P” indicates Cu_3P (cubic); and “ δ ” indicates $\text{Cu}_{41}\text{Sn}_{11}$ (cubic)

spectroscopy (EDS) and X-ray diffraction (XRD; LabX XRD-6000, Shimadzu Scientific Instruments).

3 Results and Discussion

3.1 Micromorphology change of crystal and amorphous filler metal during heating

Figures 1 and 2 show the microstructural evolution of the crystalline and amorphous filler metals, respectively, during the heating process, as measured in the high-temperature metallographic microscope. It can be seen from Figure 2 that the microstructure of the amorphous filler metal changes significantly, and especially compared with the crystalline filler metal during heating (Figure 1). For the amorphous filler metal, when the temperature reached 450°C (Figure 2b), micro-scale bumps began to appear on the solder surface that grew with increasing temperature (Figure 2c), where the interface between the bumps gradually fused at 550°C (Figure 2d). When the temperature reached 600°C , the brazing filler metal surface was essentially planar (Figure 2e). As the amorphous filler metal transforms from amorphous to crystalline during the heating process, its internal lattice structure will experience reconstruction that will change its surface morphol-

Figure 4: DSC curves of the amorphous and crystalline filler metals

ogy. However, the internal structure of crystalline filler metal is in a stable state, and therefore no significant changes were observed by optical microscopy during the heating process (Figure 1).

3.2 Microstructure and phase analysis of amorphous filler metal during heating

Although the brazing filler metal used herein was a quaternary alloy, the lattice constants of the Ni and Cu constituents are similar, as are their atomic number and structure. Moreover, Ni and Cu have infinite solubility. Therefore, we can simplify and consider the quaternary alloy a Cu-Sn-P ternary alloy. Figure 3 shows the pseudo-binary phase diagram of the Cu-P-Sn alloy, wherein “F” indicates $\text{Cu}_{13.7}\text{Sn}$, where the solid solution of copper is a face-centered cubic structure; “B” indicates the $\text{Cu}_{5.6}\text{Sn}$ compound, which is a body-centered cubic structure; “P” is a cubic structure indicating the Cu_3P compound; and “ δ ” is a cubic structure indicating the $\text{Cu}_{41}\text{Sn}_{11}$ compound. It can be seen from Figure 3 that, when the Sn content in the brazing filler metal is 10% wt and the P content is 6.5% wt, the brazing filler metal is a eutectic structure.

In the DSC curve of the brazing filler metal given in Figure 4, it can be seen that the thermodynamic characteristics during heating and the melting phase of the amorphous and crystalline brazing filler metals are nearly the same, where both types of brazing filler metals exhibit an endothermic reaction at the melting point. From Figure 3 we can deduce that two reactions occur during the heat absorption of these brazing filler metals, given as

Figure 5: Microstructure of the (a) amorphous and (b) crystalline filler metals after brazing at 380°C, (dwell time=10 min)

Figure 6: X-ray diffraction of the crystallization of amorphous filler metal during heating at (a) 380 and (b) 580°C

where F is $\text{Cu}_{13.7}\text{Sn}$, B is $\text{Cu}_{5.6}\text{Sn}$, P is Cu_3P , δ phase is $\text{Cu}_{41}\text{Sn}_{11}$.

During the brazing heating process, the amorphous filler metal crystallizes when the crystallization temperature is reached. Subsequently, after reaching the melting temperature the filler metal flows and fills the brazing seam and ultimately completes the brazing. Therefore,

in summary, the brazing mechanism of these two brazing filler metals is the same, though the microstructures of the amorphous and crystalline filler metals are different. Because the crystallization of the filler metal is a non-equilibrium phase transformation, the amorphous filler metal can complete the nucleation and grain growth in the solid state. The growth of grains in the solid state is slow owing to the difficulty for atom diffusion, and thus the grains share the same probability for nucleation. Herein, the degree of spontaneous nucleation in the amorphous filler metal was large and the grain growth was mainly equiaxed crystal. Meanwhile, the grain growth was dominated by dendrites and there was evidence of segregation resulting from the relationship of the degree of supercooling.

Figure 5 shows the microstructure of the brazing filler metal after heating to 380°C and a dwell time of 10 min. It could be seen from Figure 5 that the microstructure of the amorphous filler metal after it reached the crystallization temperature (Figure 5a) is obviously different from that of the crystalline solder (Figure 5b). In these microstructures, the amorphous filler metal exhibits a eutectic lamellar structure and the crystalline filler metal, although also a eutectic alloy, undergoes an alloy solidification process that was carried out slowly. In the crystalline filler metal (Figure 5b), the Cu_3P as the primary phase was formed initially, as well as the stripe-shaped Cu solid solution, around which were dispersed fine black particles. In other words, although the crystalline filler metal was a eutectic alloy, it could not solidify immediately during the casting and solidification. Instead, the Cu_3P was formed initially, whereupon the eutectic reaction occurred in their interstices to eventually solidify.

The amorphous filler metal was rapidly cooled in the liquid state, whereupon the liquid filler metal was so-

Figure 7: Microstructure of the brazed joints with the (a) amorphous and (b) crystalline filler metal at the brazing temperature of 650°C

Figure 8: Tensile strength of joints formed with amorphous and crystalline filler metal vs. dwell time (brazing temperature=680°C)

lified without being diffused (Figure 5a). As a result, an amorphous structure with "remote disorder and short-range order" was formed. During the heating process, the amorphous structure nucleated before the liquidus, whereupon nucleation grew. However, the diffusion of elements was slow when the amorphous core was formed in the solid phase, and the coarse cast structure was not formed owing to the high degree of uniformity of the internal structure of the amorphous brazing filler metal. During the heating process of the amorphous filler metal, no "temperature fluctuation" nor "concentration fluctuation" occurred during the growth process of the grains, which therefore grew in the form of equiaxed crystals and generated very fine microcrystals.

Figure 6 shows the XRD patterns of the amorphous filler metal at 380 and 580°C. It can be seen in Figure 6b that a $\text{Cu}_{13.7}\text{Sn}$ solid solution, a $\text{Cu}_{88}\text{Sn}_{22}$ phase and a

Ni_{12}P_5 phase were formed in the amorphous brazing filler metal when the brazing temperature was 580°C, which were absent in the composition of the filler metal at 380°C (Figure 6a). With the increase of brazing temperature, the solute elements Sn and P were continuously dissolved and precipitated from the supersaturated solid solution, and accumulation of the $\text{Cu}_{88}\text{Sn}_{22}$ and $(\text{Cu}, \text{Ni})_3\text{P}$ compound and $\text{Cu}_{88}\text{Sn}_{22} + \text{Ni}_{12}\text{P}_5 + (\text{Cu}, \text{Ni})_3\text{P}$ ternary eutectic occurred. The $\text{Cu}_{88}\text{Sn}_{22}$ phase and Ni_{12}P_5 phase were formed in the amorphous filler metal at the brazing temperature of 580°C; where the $\text{Cu}_{88}\text{Sn}_{22}$ phase is a product of Sn aggregation and the Ni_{12}P_5 phase and Cu_3P are products of P aggregation. Previous research by Chen *et al.* also reports similar phases in their results [18]. The phase diagrams of Cu-Sn and N-P show that the $\text{Cu}_{88}\text{Sn}_{22}$ phase and Ni_{12}P_5 phase are metastable phases, and these metastable phases can be decomposed.

The amorphous brazing filler metal crystalline structure comprises a γ -Cu solid solution and a small amount of Cu_3P compounds and, with increasing brazing temperature, the $(\text{Cu}, \text{Ni})_3\text{P}$ and Cu_xSn_y compounds begin to precipitate from the solid solution. The crystalline brazing filler metal, however, already possesses $(\text{Cu}, \text{Ni})_3\text{P}$ and Cu_xSn_y compounds at room temperature and, with increasing brazing temperature, the crystalline filler metal only exhibits a growth of these phases. Both types of brazing filler metals exhibited a difference in structure during the brazing process, from the initial nucleation to the melting.

The crystalline brazing filler metal is a eutectic composition. During the solidification process, the Cu_3P solder crystal was initially formed because of undercooling, whereupon the eutectic reaction occurred in the Cu_3P interstices until the ultimate solidification. The Cu_3P inter-

Figure 9: Tensile fracture morphology of the brazed joints comprising (a) amorphous and (b) crystalline filler metal (brazing temperature=680 °C, dwell time=15 min)

Figure 10: XRD patterns of a tensile fracture in brazing joint of the (a) amorphous and (b) crystalline brazing filler metal

metallic compound can reduce the joint strength and have a serious effect on the impact properties of the joint.

However, there existed no Cu_3P primary crystal in the amorphous solder during the heating process, wherein the crystalline filler metal nucleated and grew in the liquid state while the amorphous filler metal nucleated and grew in the solid state. The nucleation and growth of the amorphous alloy depended on the movement of the atoms in the solid phase. Because atomic motion in the solid phase is much slower than that in the liquid phase, the atoms seldom exhibited a wide range of motion and migrated only in a relatively small area. Therefore, segregation of elements in the solder could be effectively avoided. The amorphous filler metal began nucleating only after crystallization owing to the lack of undercooling and of a temperature gradient in the amorphous solder. The grain growth was uniform around the grain, without segregation, and a

fine grain was obtained. This type of grain can effectively increase the strength and toughness of a brazed joint.

3.3 Analysis of the microstructure and phase of the braze welds

Figure 7 shows the morphology of the brazed joints of both amorphous and crystalline filler materials. It can be clearly seen from Figure 7 that the brazing seam consists of two parts: a diffusion and dissolution layer and a brazing residual layer. The thickness of the diffusion and dissolution layer determines the degree of interaction between the brazing material and the base metal, which greatly contributes to the performance of the brazed joint. The brazing residual layer, however, is the solder that has not yet reacted with the braze joint interface and is formed during

Figure 11: Energy-dispersive spectra elemental line scan results of the brazing joint of the crystalline filler metal at 660°C, showing the (a) line scan position on the micrograph, and the distribution of the (b) Cu, (c) P, (d) Sn and (e) Ni elements along the line scan

the cooling and solidification process. Because the brazing residual layer is a region where a large number of brittle compounds accumulate, the performance in this region is often significantly degraded, and thus the thickness of the brazing residual layer has a great influence on the performance of the brazed joint.

The tensile strengths of the amorphous and crystalline filler metal joints brazed at the same temperature as a function of brazing dwell time is shown in Figure 8.

It can be seen from Figure 8 that the tensile strength of the joint increases with the dwell time, where a dwell time of 20 min exhibits the maximum strength of the brazing joint of the amorphous filler metal. Further, for the crystalline filler metal, the tensile strength of the brazed joint did not increase significantly for dwell times greater than 25 min. This indicates that the brazing time of the amorphous filler metal can be shorter than that of the crystalline filler metal.

Figure 12: Energy-dispersive spectra elemental line scan results of the brazing joint of the amorphous filler metal at 660°C, showing the line scan position on the micrograph, and the distribution of the (b) Cu, (c) P, (d) Sn and (e) Ni elements along the line scan

Figure 9 shows the tensile fracture morphology of the amorphous and crystalline filler metals after a dwell time at 680°C for 15 min, followed by cooling in the furnace. As can be seen in Figure 9, a certain number of pores are formed by the volatilization of the phosphorus elements on the tensile fractures of both types of solder, where the porosity of the amorphous solder (Figure 9a) is sig-

nificantly smaller than that of the crystalline solder (Figure 9b). The amorphous brazed joints are thus denser than the crystalline braze in the fracture morphology. Owing to the presence of pinholes in the crystalline solder, the brazed joints are completely fused, which will reduce its effective area and thereby reduce the tensile strength of the entire brazed joint. Therefore, the tensile strength of

the amorphous solder is greatly superior to that of the crystalline solder.

Figure 10 shows the XRD patterns of the tensile fracture in the amorphous and crystalline filler metal brazed joints, in which the diffusion and dissolution layer is mainly composed of γ -Cu(Sn, Ni), and the brazing residual layer is mainly composed of $[(\text{Cu}_3\text{P}+\text{Ni}_3\text{P})+\gamma\text{-Cu}(\text{Sn}, \text{Ni})]$ eutectic mixture composition. It was found that the bulk continuous gray block (Region A in Figure 7a) in the brazing residual layer of the amorphous brazing solder mainly comprises the brittle compound Cu_3P , while the brazing residual layer of the brazing of the crystalline filler metal is also scattered with Ni_3P (Region B in Figure 7b) fragility in addition to large regions comprising Cu_3P brittle compounds. The bright white feature (Region B in Figure 7a) and the bright grey area (Region C in Figure 7b) comprise γ -Cu (Sn, Ni), which is a solid solution with strong plasticity that improves the mechanical properties of the joint. Therefore, to improve the performance of the final brazing joint, it should exhibit narrower regions comprising the two brittle compounds of Cu_3P and Ni_3P in the brazed joints and wider regions comprising the Cu-based solid solution of γ -Cu (Sn, Ni) phase. To further reveal the relationship between the elemental distribution and the brazing temperature of the two brazing joint types, the tests were performed at the brazing temperatures 660 and 680°C, whereupon the elements of the brazing joints were analyzed with EDS, as shown in Figures 10 and 11.

From the results of the EDS line scan shown in Figure 10c, the phosphorus in the brazing joint is mainly concentrated in the center residual layer of the brazing seam. This is because phosphorous, which has a lower melting point, melts first during the temperature increase and begins to solidify after the brazing temperature is reached. The Cu, Ni, Sn and other elements in the molten solder initially solidify, whereupon the phosphorus element is displaced in the liquid state to the center of the brazing joint. During the cooling process, the phosphorus slowly collects toward the center of the brazing joint and, after the brazed joint is solidified and crystallized, ultimately remains in the brazing residue layer.

4 Conclusions

1. The amorphous brazing filler metal crystallized and grew under a solid state during the brazing process, exhibiting a fine grain and uniform structure. It was mainly composed of equiaxed grains without macro- or micro-segregation, which was conducive to ele-

mental diffusion and to the formation of a liquid phase during brazing.

2. The elemental activation energy of the crystalline solder was high while elemental diffusion was slow and almost unchanged in the solid state. Therefore, the crystalline filler metal scarcely changed before reaching brazing temperature during the heating process. Elemental diffusion in the amorphous filler metal was much greater than that in the crystalline filler metal and the diffusion activation of the element was less than that of the crystalline filler metal during the heating process.
3. The amorphous filler metal formed a γ -Cu solid solution and a small amount of Cu_3P compounds during the heating process of the first crystallization. With increasing brazing temperature, the solute elements Sn and P were continuously dissolved and precipitated from the supersaturated solid solution, inducing the accumulation of the $\text{Cu}_{88}\text{Sn}_{22}$ and $(\text{Cu}, \text{Ni})_3\text{P}$ compounds and $\text{Cu}_{88}\text{Sn}_{22}+\text{Ni}_{12}\text{P}_5+(\text{Cu}, \text{Ni})_3\text{P}_3$ ternary eutectic. The crystalline brazing filler metal began to melt into a liquid phase at the melting temperature.
4. The brazing joint is mainly divided into a diffusion layer and a brazing residual layer, wherein the former is mainly composed of γ -Cu(Sn, Ni) and the latter is mainly composed of $[(\text{Cu}_3\text{P}+\text{Ni}_3\text{P})+\gamma\text{-Cu}(\text{Sn}, \text{Ni})]$ eutectic mixture composition.
5. The melting point of phosphorus in the brazing seam is lower than the other elements, and thus first begins to melt during the heating process. When solidification begins after the brazing temperature is reached, Cu, Ni, Sn and other elements in the molten brazing material first solidify, and the phosphorus element is displaced in liquid form to the brazing seam. During the cooling process, phosphorus is slowly collected the center of the braze joint and, after the braze joint is solidified and crystallized, ultimately remains in the brazing residual layer.

References

- [1] L. Tian, W. H. Li, M.X. Chen, and B. Fang, *Hot Work Technol.*, 15 (2015) 158-161.
- [2] C.Z. Xia, J. Yang, X.P. Xu, and J.S. Zou, *High Temp Mater. Process.*, 36 (2017) 477-483.
- [3] A. G. Tiagunov, V. S. Tsepelev, and G. V. Tiagunov, *Mater. Sci. Forum.*, 870 (2016) 108-213.
- [4] F. Wang, S. Yin, and Z. Wang, *Spec. Cast. Nonferrous Alloys.*, 2 (2015) 335-340.

- [5] C.Z. Xia, W.W. Sun, and M.J. Zhao, *Mater. Process. Technol.*, 259 (2018) 15-22.
- [6] A.A. Ivannikov, V.T. Fedotov, O.N. Sevryukov, B.A. Kalin, A.N. Suchkov, I.S. Logvenchev, et al., *Weld.Int.*, 27 (2013) 660-664.
- [7] C. Peng, Y.D. Yuan, and W.H. Li, *Hot.Work.Technol.*, 21 (2016) 162-165.
- [8] P.I. Burak, A.V. Serov, and R.A. Latypov, *Weld. Int.*, 26 (2012) 1-5.
- [9] W.Y. Yu, X.D. Chen, W.J. Lu, *Rare Met. Mater. Eng.*, 38 (2009) 1627-1629.
- [10] C.Z. Xia, W.W. Sun, Y.J. Zhou, and X. Xu, *Alloys Compd.*, 741 (2018) 155-160.
- [11] Y.H. Liu, J.D. Hu, P. Shen, X.H. Han, and J.C. Li, *Mater. Des.*, 47 (2013) 281-286.
- [12] O.N. Sevryukov, A.N. Suchkov, and E.V. Guseva, *Non-Ferrous Met.*, 1 (2015) 45-49.
- [13] R.W. Hua, H.W. Zuo, and J.S. Zou, *Weld.Technol.*, 40 (2011) 9-12.
- [14] X.Z. Wang, *Steel Res.*, 04 (1991) 86-92.
- [15] A. Rabinkin, E. Wenski, and A. Ribaudo, *Weld. J.*, 77 (1998) 66-75.
- [16] X.P. Xu, Q.M. Liu, C.Z. Xia, and J.S. Zou, *High Temp Mater. Process.*, 37(6) (2018) 597-602.
- [17] P. He, J.H. Zhang, R.L. Zhou, X.Q. Li, *Mater. Charact.*, 43(5) (1999) 289-292.
- [18] W.Y. Yu, X.D. Chen, W.L. Lu, *Rare Metal Mat Eng.*, 38(9) (2009) 1626- 1629.