Rare Metal Materials and Engineering
Volume 50, Issue 10, October 2021
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Dong Bowen, Zhong Sujuan, Pei Yinyin, et al. Properties of Cu-P Brazing Filler Metal After Hot-Dip Tinning[J]. Rare Metal Materials and Engineering, 2021, 50(10): 3527-3531.

ARTICLE

Properties of Cu-P Brazing Filler Metal After Hot-Dip Tinning

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Abstract: The CuPSn brazing filler metal was prepared on the basis of Cu93P brazing filler metal by hot-dip tinning. The interface morphology of tin coating was observed by scanning electron microscope. The tensile strength, microhardness, melting temperature and wettability of the brazing filler metal were investigated by universal mechanical testing machine, micro-hardness tester, differential thermal analyzer, resistance furnace and stereomicroscope. The results indicate that the liquid tin reacts with the brazing filler metal to form Cu_6Sn_5 intermetallic compound during hot-dip tinning, which means that the brazing filler metal and tin coating form good metallurgical bonding. The tensile strength and microhardness of brazing filler metal decrease with the increase of hot-dipping temperature and time. The decrease of tensile strength is due to the formation of Cu_6Sn_5 brittle compound and pores at the interface, and the decrease of microhardness is due to the stress-relieving annealing effect of hot-dip. Hot-dip tinning can reduce the melting temperature and improve the wettability of the brazing filler metal. The wetting area of brazing filler metal increases by about 43.15% compared with that of the matrix when 5.20wt% tin is hot dipped in it, and the Cu88.16P6.64Sn5.20 brazing filler metal possesses a good wettability.

Key words: hot-dip; chemical affinity; melting temperature; wettability

Pure copper is an important functional material of non-ferrous metals, which has excellent conductivity, heat conduction, corrosion resistance and processing performance, but the high melting temperature greatly restricts its application in the field of brazing[1,2]. The addition of phosphorus to copper can significantly reduce its melting temperature and improve its brazing performance. Cu-P series filler metals are widely used for brazing copper and copper alloys, silver and silver alloys, molybdenum and molybdenum alloys[3].

The addition of silver in Cu-P alloy can further reduce its melting temperature and improve its processability. Therefore, Cu-P-Ag filler metal has become the most widely used filler metal for Cu-P series filler metals in refrigeration, motor and other industries. However, silver is a rare metal with limited resources. On the premise of ensuring the performance of brazing filler metal, replacing silver with other elements has become a hot research topic [4].

The melting point of tin is 231.89 ℃, which is much lower than that of copper. Tin can be added into Cu-P filler metal to reduce the melting temperature. The formability of Cu-P-Sn prepared by a traditional melting method is poor when the content of tin is more than 4.0%. It can only be used as cast rod, powder or amorphous foil, so the application range is greatly limited. With the development of remanufacturing technology and brazing technology, new manufacturing technology can be used to improve the quality and performance of brazing filler metal [5-10]. The author applied the hot-dip technology to the preparation of CuZnSn filler metal in the early stage, and achieved good results[11]. However, to prepare Cu-P-Sn filler metal with no silver and high tin content using hot-dip tinning has seldom been reported.

The hot-dip technology was used to improve the brazing performance of filler metal in this work. The CuPSn brazing filler metal was prepared on the basis of Cu93P brazing filler metal by hot-dip tinning. The effect of hot-dip tinning process on the properties of Cu93P filler metal was discussed. The

Received date: October 23, 2020
Foundation item: Science and Technology Major Project of Zhengzhou City (2019CXZX0065); Leading Talents of Science and Technology in Central Plains (ZYQR20180030)
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interface morphology between tin coating and the substrate, the mechanical properties, melting temperature and wettability of CuPSn filler metal were investigated.

1 Experiment

The base material used in this experiment was strip-shaped Cu93P filler metal (*Φ*2.5 mm×1000 mm), and the chemical composition was 93.04wt% Cu and 6.96wt% P. The hot-dip tinning process was carried out in a self-made test device, and the principle is shown in Fig.1. The composition of flux (wt%) was $52ZnCl_2$+$48NH_4Cl$. The hot-dip temperature was 250, 270, 290, 310 and 330 ℃. The hot-dip time was controlled by adjusting the drawing speed of Cu93P filler metal, and the hot-dip time was 10, 20 and 30 s. The tin content of brazing filler metal was controlled by adjusting the size of drawing die aperture. The etchant was used to remove tin layer on the surface of Cu93P filler metal to expose the interface compound grains, and the etchant was composed of 5%HCl+ 3%HNO_3+CH_3OH. The microstructure and micro fracture morphology of the samples were observed by scanning electron microscope (SEM). The tensile test of samples was referred to "GB /T228.1-2010 Tensile Test of Metallic Materials Part 1: Test Method at Room Tempe-rature", and the tensile strength of samples was tested at the speed of 10 mm/min by MTS C45.105 electronic universal testing machine. The tensile strength of the samples was the average of 5 samples. The microhardness of the samples was analyzed by HV-1000A microhardness meter. The load was 100 g, and the loading time was 10 s. At least 10 points were selected for each sample, and the arithmetic mean value was taken as the microhardness of the substrate. The influence of tin content on the melting temperature of filler metal was analyzed by differential scanning calorimetry (DSC). The equipment was STA449F3 produced by Netzsch company of Germany. The test process was completed in an alumina crucible under nitrogen atmosphere. According to the melting temperature of Cu-P brazing alloy, the scanning temperature ranged from 30 ℃ to 850 ℃. The heating rate was 15 ℃/min, and the temperature measuring accuracy was ±0.5 ℃. The scanning results of DSC were analyzed by Proteus software. Test method of wettability for brazing filler metals was referred to GB/T11364-2008 test method of wettability for brazing filler metals. Before the wetting test, the pure copper plate (4 cm×4 cm×0.2 cm) should be polished by 100# and 400# sandpaper to ensure that the surface of the plate was smooth, and then it was cleaned with CH_3OH. Afterwards 200 mg of brazing filler metal was placed in the center of the pure copper plate and covered with FB102 flux. The samples were heated in SX2-10-12G resistance furnace. Then they were held for 40~50 s after the filler metal was melted, and then cleaned after natural cooling at room temperature. The spreading samples were scanned in SteREO Discovery. V8, and the wetting area of brazing filler metal was calculated.

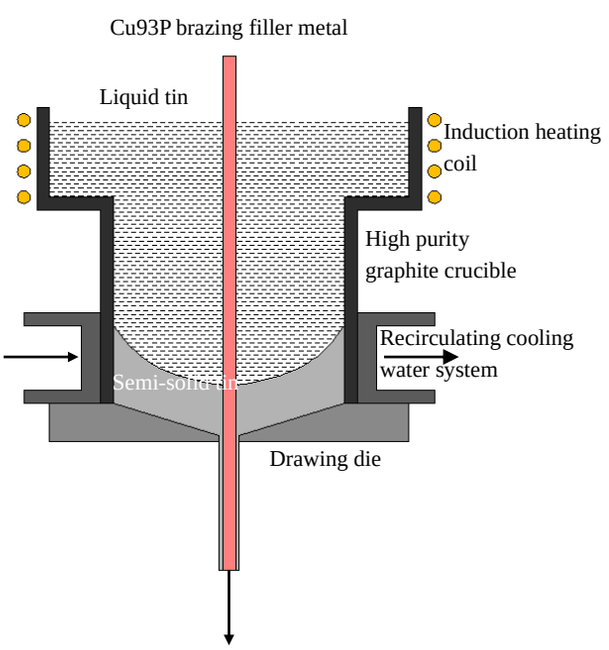

Fig.1 Principle of hot-dip tinning for Cu-P brazing filler metal

2 Results and Discussion

2.1 Microstructure

Fig. 2 shows the interface morphology between tin coating and Cu93P filler metal when the hot-dip temperature is 250 ℃ and the hot-dip time is 10 s. It can be seen from Fig.2a that the tin coating is uniform, flat and dense. A rod-shaped continuous compound layer is formed at the interface, and the surface morphology of the interface compound is shown in Fig. 2b. The interaction between tin and the elements in Cu93P filler metal can be characterized by chemical affinity. The larger the chemical affinity between two elements, the more easily the compounds are formed. On the contrary, the lower the chemical affinity, the less likely the compounds will be formed[12].

The chemical affinity between two elements can be calculated by Eq.(1)[12],

$$\eta = \left(\frac{Z}{r_K}\right)_A \Big/ \left(\frac{Z}{r_K}\right)_B + \Delta X \quad (1)$$

where η is the chemical affinity parameter, Z/r_K is the ratio of

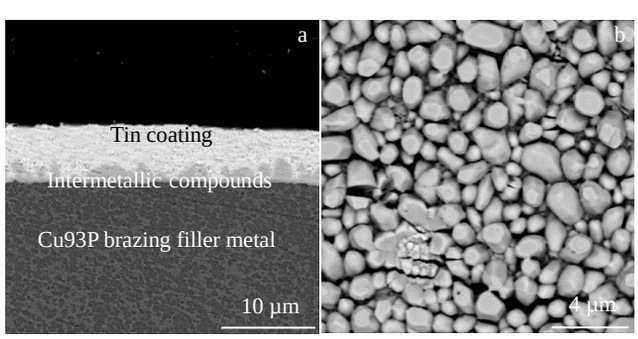

Fig.2 Interface morphologies between tin coating and Cu93P filler metal (a) and surface morphology of the rod interface compound (b)

the charge number of element to the atomic radius, and ΔX is the difference between X_A and X_B which is the electronegativity of elements. It should be noted that the equation of $(Z/r_K)_A/(Z/r_K)_B$ always takes the smaller (Z/r_K) as the denominator, so the value of $(Z/r_K)_A/(Z/r_K)_B$ is always greater than 1.

The chemical affinity parameters of Cu-Sn and P-Sn can be calculated according to Eq. (1), as shown in Table 1. The results in Table 1 show that the chemical affinity parameter of tin to copper is greater than that to phosphorus. The greater the chemical affinity between two elements, the more likely the formation of compounds[13]. It can be seen that the tendency to form Cu-Sn compound is greater than that to form P-Sn compound at the interface during hot-dip tinning, so tin and copper are more likely to interact to form Cu_6Sn_5 intermetallic compound[14]. This is consistent with the results of energy spectrum analysis, as shown in Table 2.

2.2 Mechanical Properties

2.2.1 Tensile strength

The effect of different hot-dip temperatures and time on the tensile strength of filler metal is shown in Fig.3. When the hot-dip temperature is higher than 250 ℃, the tensile strength of filler metal decreases significantly compared with Cu93P brazing filler metal with the increase of hot-dip temperature. The tensile strength of filler metal decreases with the extension of hot-dip time at the same hot-dip temperature. The initial tensile strength of Cu93P brazing filler metal is 783.34 MPa. The tensile strength of brazing filler metal remains unchanged with the extension of hot-dip time when the hot-dip temperature is 250 ℃, which indicates that Cu93P brazing filler metal maintains good thermal stability when hot-dip tinning is performed at 250 ℃. Cu93P brazing alloy is hypoeutectic according to the Cu-P phase diagram, which is composed of $\alpha_{(Cu)}$ plastic phase and Cu_3P brittle phase. The dispersed Cu_3P brittle phase improves the tensile strength of $\alpha_{(Cu)}$. Both $\alpha_{(Cu)}$ and Cu_3P maintain good thermal stability at 250 ℃, quasi-cleavage fracture occurs during the tensile process, and a large number of dimples and tearing edges appear on the fracture surface, as shown in Fig. 4a. The tensile strength of filler metal decreases greatly when the hot-dip temperature is 270 ℃ or above. The tensile strength of filler metal is 569.14 MPa when the hot-dip temperature is 270 ℃ and the hot-dip time is 10 s, which is about 27.34% lower than that of Cu93P filler metal. Cleavage fracture occurs during tensile process, as shown in Fig. 4b. The sharp decrease of tensile strength is due to the formation of a large amount of Cu_6Sn_5 brittle compound along the cross-section of the filler metal during hot-dip tinning. Cu_6Sn_5 brittle compounds are connected with Cu_3P brittleness, which become new crack sources, as shown in Fig. 5. When the hot-dip temperature is 290 ℃ and the hot-dip time is 10 s, holes begin to appear at the interface, as shown in Fig. 6a. These holes increase the crack sources, and the tensile strength of solder decreases. The holes increase in amount with the increase of hot-dip temperature to 310 ℃, as shown in Fig. 6b, and the tensile strength of filler metal further decreases.

2.2.2 Microhardness

The effect of different hot-dip temperatures and time on the microhardness of the filler metal is shown in Fig. 7. The microhardness of the filler metal after hot-dip tinning decreases obviously. The initial microhardness of Cu93P filler metal is 1961 MPa. The microhardness of the filler metal is 1755 MPa when the hot-dip temperature is 250 ℃ and the hot-dip time is 10 s, and it is decreased by 10.51% compared to that of the matrix. The microhardness of the filler metal is 1532 MPa when the hot-dip temperature is 330 ℃ and the hot-dip time is 10 s, which is 21.89% lower than that of the matrix. The microhardness of the filler metal gradually decreases as the hot-dip temperature increases, and the microhardness of the filler metal slowly decreases with the

Table 1 Chemical affinity parameters between copper, phosphorus and tin

Chemical element	$(Z/r_K)_A$	$(Z/r_K)_B$	X_A	X_B	ΔX	η
Cu-Sn	5.64	1.04	1.96	1.90	0.06	5.48
P-Sn	14.7	5.64	2.19	1.96	0.23	2.84

Table 2 Element content of compound layer at the interface

Cu content/wt%	Sn content/wt%	Phase
37.58	62.42	Cu_6Sn_5

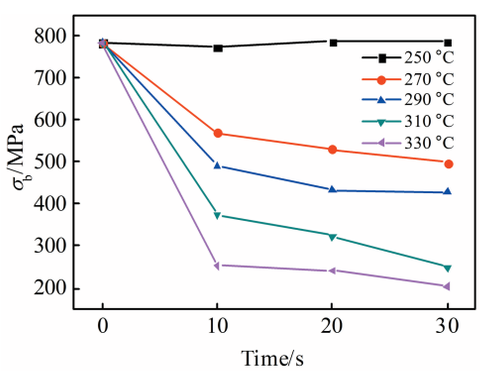

Fig.3 Effect of hot-dip temperature and time on tensile strength of Cu973 brazing filler metal

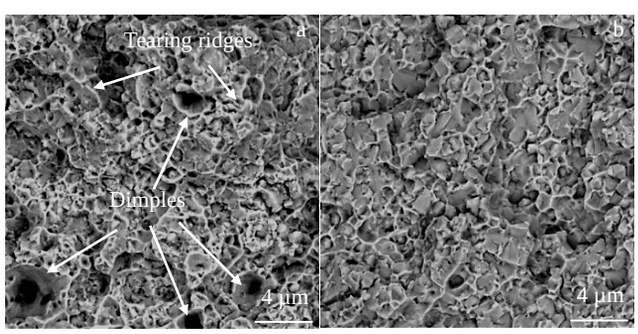

Fig.4 Fracture morphologies of Cu93P brazing filler metal after hot-dip tinning: (a) 250 ℃, 10 s; (b) 270 ℃, 10 s

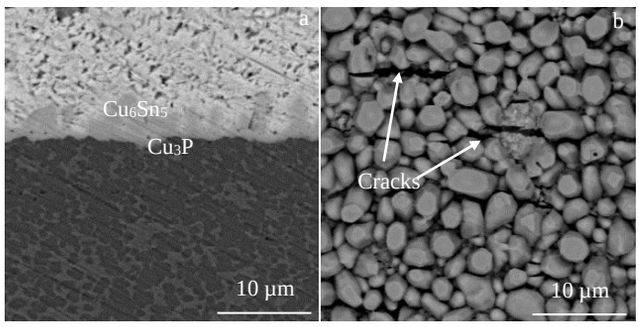

Fig.5 Interfacial reaction between tin coating and Cu93P filler metal

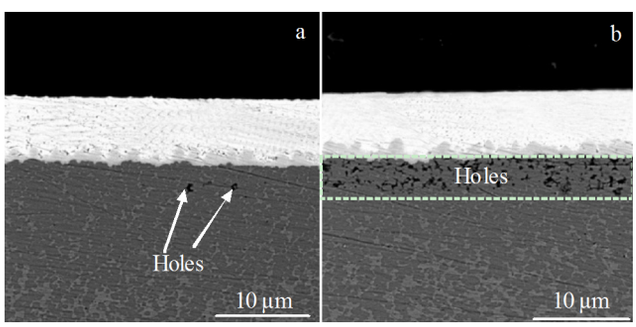

Fig.6 Microstructures of filler metal in longitudinal section under different hot-dip parameters: (a) 290 °C, 10 s; (b) 310 °C, 10 s

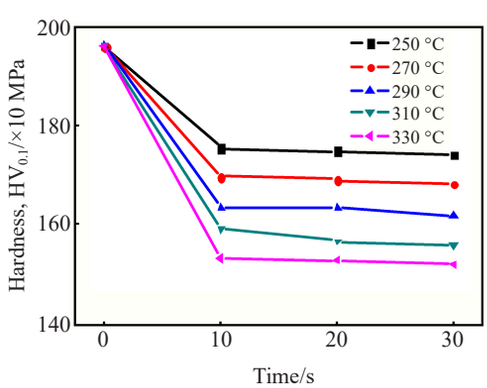

Fig.7 Effect of hot-dip temperature and time on the microhardness of filler metal

extension of the hot-dip time. This is mainly due to the fact that the Cu93P filler metal is drawn and straightened, and these processes have an effect of work hardening. The hot-dip tinning exerts a stress-relieving annealing effect on the Cu93P filler metal, and the microhardness of the filler metal decreases. The higher the hot-dip temperature or the longer the hot-dip time, the stronger the stress-relieving annealing effect of the matrix, and the lower the microhardness[15].

2.3 Melting temperature and wettability

Fig. 8 shows the DSC curves of Cu93P brazing filler metal before and after hot-dip tinning. The solidus temperature and liquidus temperature of the solder are set as the starting point temperature and the ending point temperature of the endothermic peak on the DSC curve, respectively. The characteristic temperature of endothermic peak corresponding to the filler metal in Fig. 8 is shown in Table 3. The melting temperature of Cu93P filler metal ranges from 721.05 ℃ to 736.31 ℃, and that of Cu88.16P6.64Sn5.20 filler metal ranges from 660.51 ℃ to 695.78 ℃. The solid and liquid phase lines of Cu93P filler metal after hot-dip tinning decrease, which means that hot-dip tinning on the surface of Cu93P filler metal can reduce the melting temperature.

The brazability was evaluated by the wettability. The wettability comparison between Cu93P filler metal and Cu88.16P6.64Sn5.20 filler metal after hot-dip tinning is shown in Fig. 9. The wetting area of Cu88.16P6.64Sn5.20 filler metal increases by 43.15% compared to that of Cu93P after 5.20wt% tin is hot dipped in it. The reason is that actual liquid metal is viscous liquid whose flow performance can be measured by the viscosity of liquid metal. The viscosity is

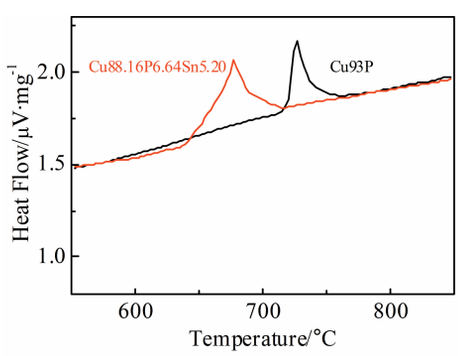

Fig.8 DSC curves of brazing filler metals

Table 3 Characteristic temperature of endothermic peak in Fig.8 (°C)

Specimen	Solids, T_S	Liquidus, T_L	Temperature range, ΔT
Cu93P	721.05	736.31	15.26
CuPSn	660.51	695.78	35.27

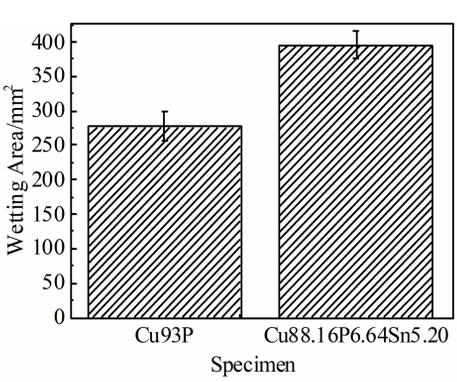

Fig.9 Wettability of Cu93P and Cu88.16P6.64Sn5.20 brazing filler metals

inversely proportional to the superheat of liquid metal. Therefore, when the brazing temperature is fixed, the lower the melting temperature of the filler metal, the higher the superheat of the liquid filler metal, which causes the decrease of viscosity of the liquid metal and the increase of fluidity[16-18]. Tin is a low melting-point element which can reduce the melting temperature of the filler metal and increase the superheat, and then the wettability and spreading properties of the filler metal can be improved.

3 Conclusions

1) The liquid tin can react with the brazing filler metal to form Cu_6Sn_5 intermetallic compound during hot-dip tinning, which means that the brazing filler metal and tin coating form good metallurgical bonding.

2) The tensile strength and microhardness of brazing filler metal decrease with the increase of hot-dipping temperature and time. The decrease of tensile strength is due to the formation of Cu_6Sn_5 brittle compound and pores at the interface, and the decrease of microhardness is due to the stress-relieving annealing effect of hot-dip.

3) Hot-dip tinning can reduce the melting temperature and improve the wettability of the brazing filler metal. The wetting area of brazing filler metal increases by about 43.15% compared with the matrix when 5.20wt% tin is hot dipped, and the Cu88.16P6.64Sn5.20 brazing filler metal possesses a good wettability.

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热浸镀锡铜磷钎料的性能

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摘　要：以Cu93P钎料为基体，在其表面热浸镀锡，制备CuPSn钎料，采用扫描电镜、万能力学试验机、显微硬度计、差热分析仪、箱式电阻炉和体视显微镜分析锡镀层的界面形貌，钎料的抗拉强度、显微硬度、熔化温度和润湿性。结果表明：在Cu93P钎料表面热浸镀锡过程中，液态锡与钎料发生了界面反应，生成Cu_6Sn_5金属间化合物，即钎料基体与锡镀层形成良好的冶金结合；随着热浸镀温度的升高和时间的延长，CuPSn钎料的抗拉强度和显微硬度均呈降低趋势，抗拉强度的降低源于界面处产生的Cu_6Sn_5脆性化合物和孔洞，显微硬度的降低源于热浸镀的去应力退火作用；Cu93P钎料表面热浸镀锡可降低钎料的熔化温度，提高钎料的润湿性，Cu93P钎料表面热浸镀5.20%（质量分数）锡之后，Cu88.16P6.64Sn5.20在纯铜板上的润湿铺展面积比基体Cu93P钎料增加43.15%。

关键词：热浸镀；化学亲和力；熔化温度；润湿性

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