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Dissolution behavior of Cu in Cu−Ag and Cu−P brazing alloys using weld brazing

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Abstract: The dissolution behavior of base metal Cu in the Cu−Ag and Cu−P brazing alloys using weld brazing was researched. The thickness loss of Cu foil in contact with Cu−P and Cu−Ag alloys at 800−920 °C was measured. And the dissolution rate constants in both alloys were calculated as the following relation: $k_{\text{Cu-P}}(T)=10k_{\text{Cu-Ag}}(T)$, which explains the special phenomenon that the dissolving amount of copper in Cu-P liquid alloys is larger than that in Cu-Ag alloys under the same condition. As weld brazing has its own characteristics of short reaction time and quick temperature variation in one thermal cycle, the quick dissolution rate of copper in filler metals is the main reason to achieve weld brazing. It can be concluded that element P is indispensable in filler metals compared with element Ag as the function of accelerating dissolution during weld brazing. Finally, the influences of the addition of alloy element on mechanical performance of the welding joints were studied and the design principles of filler metals for weld brazing were proposed to achieve good mechanical performance.

Key words: weld brazing; dissolution rate; temperature distribution; mechanical performance

1 Introduction

Aiming at the difficulty of preheating large dimension thick copper plate and the waste of human and material resources, a gas tungsten arc (GTA) weld brazing of thick copper plate without preheating is used to save energy source and shorten man-hour. A better weld joint shape forming and mechanical performance can be achieved by using the new weld brazing process [1−2]. But the dissolving mechanism of Cu in molten brazing alloys to achieve weld brazing technology still needs to be studied further. The dissolution of copper has been studied especially in electronic packaging [3]. But these studies emphasize on the growth kinetics of the inter-metallic compounds and the effect of element Sn in order to accelerate or decelerate the dissolution of copper bond pad [4−6].

Although the Cu−Ag−P ternary alloys were selected in weld brazing, the research of respective effect of P and Ag on molten brazing fillers still lacks. The dissolving behaviors of Cu in Cu−P and Cu−Ag alloys respectively need to be studied deeply, and it is helpful to understand the dissolving mechanism of weld brazing. The Cu−Ag−P brazing alloy is widely used in brazing technology in former research [7−9]. Element P acts as a de-oxidant or a fluxing agent and the function of increasing fluidity in liquid state, but the joint is brittle when P is more than 5% at room temperature [10]. And element Ag has effect on improving ductility of weld joints lowered by addition of element P [11]. Besides, the diffusion of Ag at grain boundary of polycrystalline Cu and in single crystals Cu under the eutectic temperature has been studied and measured [12−13], and the effects of dissolving mechanisms of element Ag and P on the eutectic temperature have not further carried out yet.

The key point to realize weld brazing is dissolving as much as possible copper in a short time. In this study, the main point is how to dissolve more copper during brazing. In this work, the dissolution rates of copper dissolved in Cu−P and Cu−Ag binary alloys were measured and calculated. The dissolving abilities of Cu in different brazing alloys were compared and the effects of elements P and Ag dissolving Cu respectively were researched in brazing alloys. Then the experiments using these two brazing alloys by arc heating were carried out to explain the basic reason of achieving weld brazing. Finally, the functions of alloy elements on mechanical performance were compared and the design principles of fillers for weld brazing were proposed.

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2 Experimental

The focus of the work is on the role of Ag and P dissolving of Cu in molten Cu-based brazing alloys during solid/liquid reaction. The brazing alloys used in this study were HL201 and HL308 and the composition is shown in Table 1. The brazing alloy baths containing 300 g alloys in crucibles in a high frequency induction were maintained at 800, 830, 870, 900 and 920 °C, respectively. The substrate metal was high-purity copper foil (99.99%) with 500 μm in thickness. The Cu specimens were dipped into a 5% H_2SO_4 solution for 10 s to remove the oxide and rinsed in de-ionized water and ethanol before testing. The Cu specimens were vertically dipped in the brazing alloy baths at different temperatures. After various durations ranging from 2 to 20 s, they were quickly taken out and quenched in water. After ultrasonic cleaning in ethanol, they were mounted in holders and embedded in epoxy, ground and polished, and finally etched to reveal the dissolving thickness of Cu specimens. Then the weld brazing test was carried out. Copper plates were heated for 30 s using argon shielded arc heating with HL201 and HL308 alloys in same condition. HL308 alloys combined with QJ301 were used during the arc heating course to remove the oxide film and prevent from the oxidation.

Table 1 Composition of filler metals

Alloy	Melting point/°C	*w*(Ag)/%	*w*(P)/%	*w*(Cu)/%
HL201	800	−	7	Bal.
HL308	780	72	−	Bal.
HL205	670	6	5	Bal.
HL204	645	15	5	Bal.

3 Results and discussion

3.1 Dissolving behavior of Cu in Cu−Ag and Cu−P brazing alloys

There is an interesting phenomenon that the consumed thickness of copper in Cu−P liquid binary alloys is lager than that in Cu−Ag liquid binary alloys (Figs. 1 and 2). It should be noticed that the consumed copper involves both sides, while in weld brazing alloys only contacts one side. From the classical phase diagram of Cu−Ag and Cu−P it can be seen obviously that the maximum dissolution quality of copper in Cu−Ag binary alloys is larger than that in Cu−P binary alloys when experimental conditions are in equilibrium state for an enough long time, which is opposite to the real dissolution phenomenon when welding brazing is used. This dissolution phenomenon is related to the processing conditions of weld brazing.

Figure 3 shows the temperature distribution of reaction interface simulated by commercial finite element software MARC. MSC when using weld brazing. The points 1, 2 and 3 were taken on behalf of the positions at the plate from center of the welds to edge of the plate, respectively. The binary alloys such as Cu−Ag and Cu−P

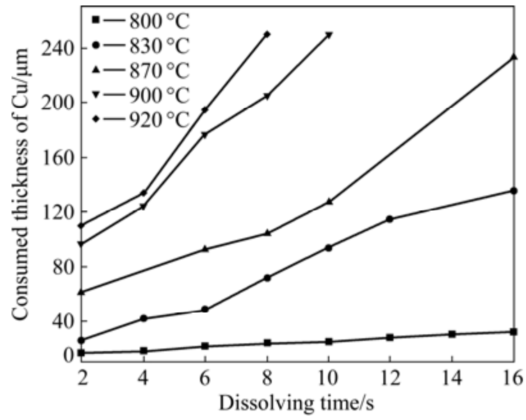

Fig. 1 Consumed thickness of Cu in Cu−P alloys at different temperatures for different time

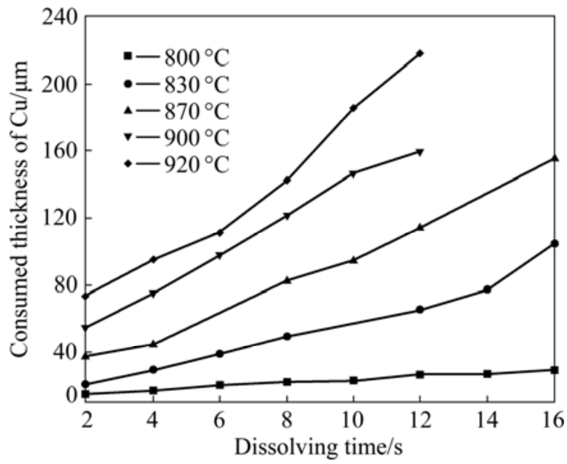

Fig. 2 Consumed thickness of Cu in Cu−Ag alloys at different temperatures for different time

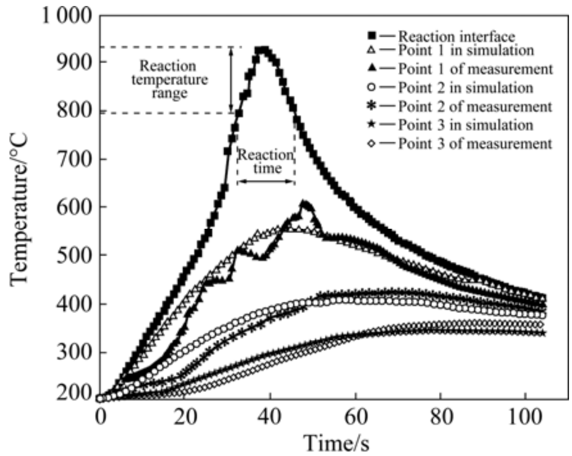

Fig. 3 Thermal cycle curves at reaction interface during one thermal cycle

were used as filler metals which have the ability to dissolve base metals upon 800 °C. Therefore, it can be seen in Fig. 3 that there is only about 20 s to reach above 800 °C at reaction interface during a thermal cycle and temperature is changed constantly with brazing time. The former research shows that when brazing copper and its alloys with transient liquid phase (TLP), the brazing time ranges from 5 min to 30 min according to different elements in filler metal to obtain the excellent joints [14−15]. While weld brazing has the characteristic of short sustained reaction time and rapid temperature variation, therefore in such a short time how to dissolve enough base metals does not depend on the maximum dissolved quantity but the dissolving rate of Cu in Cu−Ag and Cu−P liquid alloys by using weld brazing technology.

Following Dybkov's analysis, it can be seen that the dissolution of base metal is related to dissolution rate constant. Formula (1) shows that dissolution rate constant is directly proportional to consumed thickness of copper foil and density of copper and inversely proportional to density of filler metals and the term (C_s−C).

$$k=\frac{\Delta h}{\Delta t}\frac{\rho_{\mathrm{Cu}}}{\rho_{\mathrm{bm}}}\frac{1}{C_{\mathrm{s}}-C} \tag{1}$$

where k is dissolution rate constant; Δh is the dissolved thickness of copper foil; ρ_{Cu} and ρ_{bm} are densities of copper and brazing metal respectively. The dissolution rate constants of copper foil dissolved separately in Cu−P and Cu−Ag liquid binary alloys at different temperatures were calculated.

It can be found from Fig. 4 that the dissolution rate constant of copper dissolved in Cu-P alloys is faster than that in Cu−Ag alloys, that is $k_{\mathrm{Cu-P}}(T)$= $10k_{\mathrm{Cu-Ag}}(T)$. The effective diffusion coefficient of Ag diffusing into Ag−20Cu alloys at 820 °C is 7.4×10^{-8} cm^2/s [14]. As the diffusion course is the control way and the dissolution thickness is 170 μm, the dissolution rate is 0.435 μm/s, whose order of magnitude is in accordance with the calculating data shown in Fig. 4 well. The relational expression of $k_{\mathrm{Cu-P}}(T)=10k_{\mathrm{Cu-Ag}}(T)$ means that dissolving copper amount in Cu−P alloys is greater than that in Cu−Ag alloys with the same time and temperature. As the main reason to achieve weld brazing is to obtain the dissolved quality of base metal as much as possible in such a short time, element P has the ability to accelerate dissolution of copper compared with element Ag.

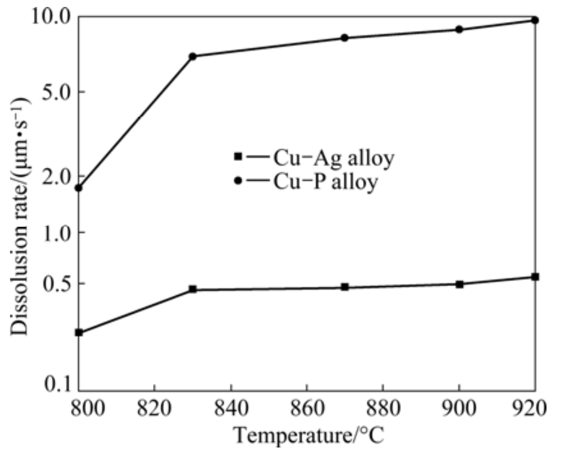

Fig. 4 Dissolution rate of Cu in Cu−P and Cu−Ag alloys in temperature range of weld brazing

3.2 Dissolving phenomena by using arc heating

The actual dissolution of base metal copper dissolved in Cu−Ag and Cu−P binary alloys was measured by using arc heating. In this experiment the arc heating time is 30 s under the same weld brazing process conditions. And HL308 alloys combined with QJ301 during the weld brazing to remove the oxidation film of copper surface. It can be obviously seen that the reaction interface moves to base metals clearly and the base metals dissolved into liquid filler metals during such a short time by using Cu−P alloys, while the reaction interface keeps almost unchanged by using Cu−Ag alloys, as shown in Figs. 5(a) and (b). And these phenomena are in accordance with dissolving behavior obtained formerly.

Figures 5(c) and (d) show the microstructures of reaction interface by using Cu−P and Cu−Ag alloys. It can be seen that the filler metal regions of Cu−P alloys are composed of α-Cu solid solution and Cu−P binary eutectic and filler metal regions of Cu−Ag alloys are composed of Cu−Ag binary eutectics. The main reason of higher dissolving rate of Cu in Cu−P than in Cu−Ag can be explained as follows. One reason is that the diffusion rate of element P in α-Cu lattice is faster than that of element Ag. On the one hand, the larger the difference of radius between diffusion element and base metal is, the faster the diffusion rate is. The radius difference of P and Cu is larger than Ag and Cu. At the reaction interface the liquid brazing filler contacts with solid copper. The element P exists as P^{3-} ion and element Ag exists as Ag atom in liquid brazing filler, element Cu exists as Cu neutral atom in base metal. The ion radius of P^{3-} is 0.17 Å and atom radius of Ag is 1.75 Å, atom radius of Cu is 1.57 Å. On the other hand, the less the solid solubility of diffusion element in base metal is, the faster the diffusion rate is. The solubility of P in α-Cu is less than that of Ag according to phase diagram, and the real solubility is shown in Table 2. The other reason is that the diffusion path is different in these two alloys. Bulk diffusion of Ag in α-Cu is only diffusion path in

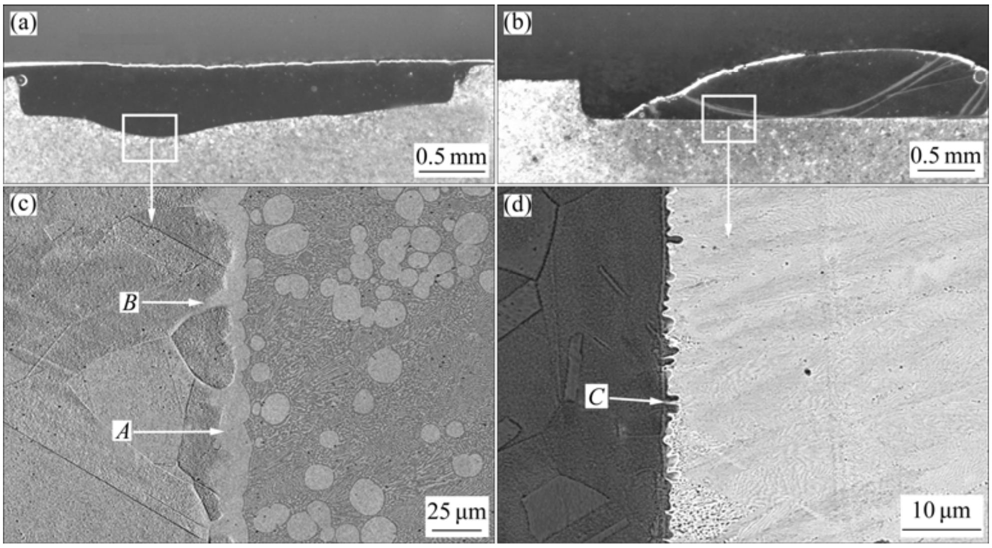

Fig. 5 Macrostructure and microstructure of interface using arc heating: (a), (c) Cu−P alloys; (b), (d) Cu−Ag alloys

Table 2 Content of elements P, Ag, Cu of positions *A*, *B* and *C*

Position	w(P)/%	w(Ag)/%	w(Cu)/%
A	1.02	−	98.98
B	0.89	−	99.11
C	−	9.74	90.26

Cu−Ag alloys, while besides the bulk diffusion of P in α-Cu, the inter-granular penetration occurred at grain boundary in Cu−P alloys. The more the diffusion path is, the faster the diffusion rate of filler metal in base metal is and the faster the dissolving rate of base metal is. According above two reasons, dissolving rate of Cu in Cu−P alloys is higher than in Cu-Ag alloys.

From the research of dissolution behavior in different time and temperatures and real dissolving phenomenon in weld brazing, it can be concluded that element P accelerates dissolution of Cu compared with element Ag. And P is the essential element in brazing metals when using weld brazing.

3.3 Microstructure and mechanical performance of welding joints

It is well known that the joint is brittle when content of P is over 5% and the Ag has the effect of improving ductility. The Cu−P−Ag ternary alloys should be selected to not only realize weld brazing but also obtain welding joint with good mechanical performance. In former research results in Refs. [1] and [2], the mechanical properties such as tensile strength, micro-hardness and bending property of the weld metal and the welding joint are good, only the impact ductility is not very good and the welded metal is little brittle. Therefore, to obtain the good ductility of the welding joint, the Cu−P−Ag ternary alloys with different contents of Ag and P are selected in weld brazing, and their chemical compositions are listed in Table 1.

The microstructures of the welds using different fillers are shown in Fig. 6. The microstructure of the welds with HL201 is composed of α-Cu and Cu−Cu_3P eutectic structure. The microstructure of the welds with HL205 is composed of α-Cu, block brittle phase Cu_3P and a small quantity of bright Ag solid solution. The microstructure of the welds with HL204 is composed of α-Cu and Cu−Cu_3P−Ag ternary structure. The different phases in microstructure of the welds would have a direct effect on the mechanical performance, especially impact ductility of the joints (Fig. 7). Figure 8 and Table 3 show the composition and micro-hardness of different phases. Vicker’s micro-hardness of the phases in the joint was measured under dynamic ultramicro-hardness tester with a loading force of 50 mN and holding time of 10 s. It could be seen that the impact ductility has an increasing tendency with the increase of Ag content in filler alloys. This is mainly because that the micro-hardness of α-Cu is decreased with increasing the content of Ag in it. The impact ductility is not improved obviously with HL205 compared with the joint with HL201. This main reason is that the amount of Ag is not enough to form ternary structure and the block brittle phase Cu_3P connects with each other when HL205 is used. Phase Cu_3P has the highest hardness among these phases shown in Fig. 8. The Cu−Cu_3P−Ag is formed and block phase Cu_3P disappears, as shown in Fig. 6(c)), when the content of Ag reaches 15%. As micro-hardness of phase Cu−Cu_3P−Ag is decreased to about HV 140, the impact ductility of the joints is improved. Therefore, two principles could be proposed to design the filler metals special for weld brazing of copper. One is decreasing the content of P to avoid the existence of block brittle phase Cu_3P on the promise of dissolving as much as possible base metal. The other is that increasing the content of Ag to form Cu−Cu_3P−Ag ternary structure or Ag solid solution. These two design principles of filler metals would be help for improving the mechanical performance of welding joints.

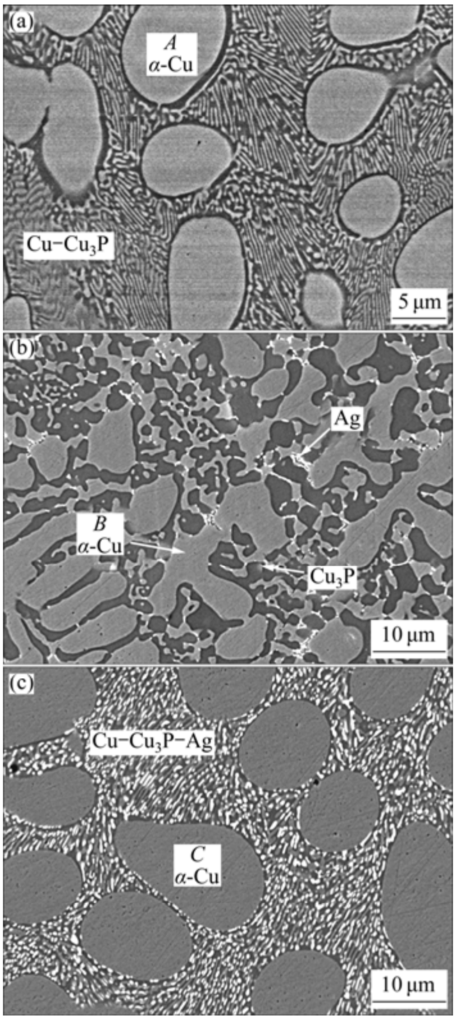

Fig. 6 Backscattered electron images of welds with different filler metals: (a) HL201; (b) HL205; (c) HL204

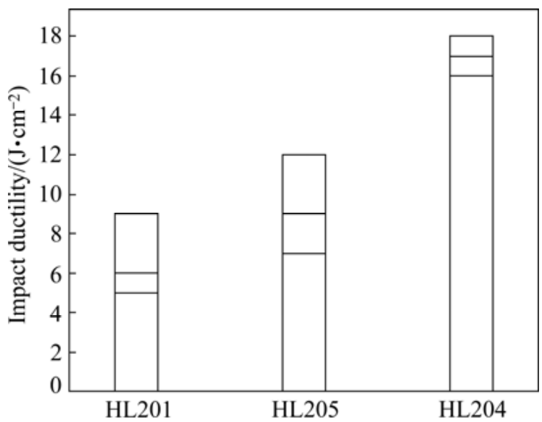

Fig. 7 Impact ductility of welding joints with different filler metals

Table 3 Composition of *α*-Cu with different filler metals

Position	*w*(Ag)/%	*w*(P)/%	*w*(Cu)/%
A	−	0.93	99.07
B	1.35	1.31	97.94
C	4.79	1.02	94.19

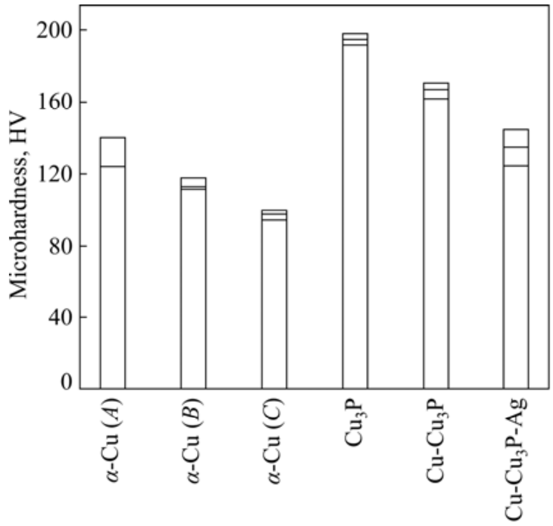

Fig. 8 Micro-hardness of different phases in welds

4 Conclusions

1) As the weld brazing has the characteristic of short reaction time and quick temperature variation, the main reason to achieve weld brazing technology is to dissolve enough base metals as quickly as possible.

2) The dissolution rates of copper dissolved in Cu−P and Cu−Ag liquid alloys are deduced as the following relationship: $k_{\text{Cu-P}}(T)=10k_{\text{Cu-Ag}}(T)$, which means that the dissolution rate in Cu−P alloys is faster than that in Cu−Ag alloys in the same condition. Element P in filler metals has the function of accelerating dissolution of copper during weld brazing compared with element Ag, and becomes the indispensable element in filler metals special for weld brazing of copper.

3) The different amount of alloy elements has great influence on mechanical performance of the welding joints and the design principles of filler metals for weld brazing of copper were proposed. One is decreasing the content of P to avoid the existence of block brittle phase Cu_3P on the promise of dissolving enough base metals. The other is increasing the content of Ag to form Cu−Cu_3P−Ag ternary structure or Ag solid solution.

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溶解钎焊时 Cu 在 Cu-Ag 及 Cu-P 合金钎料中的溶解行为

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摘　要：研究溶解钎焊条件下母材 Cu 在 Cu-Ag 及 Cu-P 合金钎料中的溶解行为。测量了在 800~920 °C 的温度范围内铜箔在 Cu-P 和 Cu-Ag 合金中的溶解厚度。推导并计算出 Cu 在这两种合金钎料中的溶解速度常数存在如下关系：$k_{\text{Cu-P}}(T)=10k_{\text{Cu-Ag}}(T)$。结果表明，采用溶解钎焊工艺时在相同条件下液态 Cu-P 合金对母材 Cu 的溶解量大于 Cu-Ag 合金的。由于溶解钎焊工艺在一个热循环内具有反应时间短和温度变化快的特点，因此 Cu 在液态钎料中快的溶解反应速度是实现溶解钎焊的根本原因。同时，P 元素与 Ag 元素相比具有加速溶解母材的作用，是实现溶解钎焊必不可少的合金元素。研究了合金元素的添加对焊接接头力学性能的影响，提出了获得良好力学性能的钎料成分设计原则。

关键词：溶解钎焊；溶解速度；温度场；力学性能

(Edited by LI Xiang-qun)