

Title	Erosion of Pure Copper by Copper Phosphorus Brazing Filler Metals containing Tin and Silver : Copper Phosphorus Brazing Filler Metals with Low Melting Temperature (Report V)(Physics, Process, Instrument & Measurement)
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Citation	Transactions of JWRI. 18(2) P.205-P.209
Issue Date	1989-12
Text Version	publisher
URL	http://hdl.handle.net/11094/4573
DOI	
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Erosion of Pure Copper by Copper Phosphorus Brazing Filler Metals containing Tin and Silver†

— Copper Phosphorus Brazing Filler Metals with Low Melting Temperature (Report V) —

Tadashi TAKEMOTO*, Ikuo OKAMOTO** and Junji MATSUMURA***

Abstract

The erosion of pure copper base metal by molten brazing filler metal was investigated using copper phosphorus brazing filler metals with low melting temperature containing tin and silver. The depths of erosion were measured at central cross section of spread test specimens. The additional elements of silver, tin and phosphorus significantly increased the erosion depth with increasing their content. Erosion depth increased linearly with square root of the holding time at 700 ~ 740°C. The activation energy of erosion of copper base metal by Cu-Sn-P filler metal coincided well with that of diffusion of tin in solid copper, suggesting the erosion reaction is controlled by diffusion of tin in solid copper. Phosphorus content has the greatest influence on the erosion depth of copper base metals among the filler metal elements.

KEY WORDS : (Erosion) (Filler metals) (Copper) (Spread test) (Silver) (Tin) (Diffusion)

1. Introduction

Phase diagrams, microstructures and spreadability have been investigated on Cu-Ag-P and Cu-Sn-P ternary alloys and Cu-Ag-Sn-P quaternary alloys, and liquidus phase planes and cross sectional phase diagrams were established¹⁻⁶). In practical use, erosion of copper base metal by copper phosphorus brazing filler metals is one of the important parameter of brazeability. Erosion reaction is the combined phenomena of dissolution of copper base metal into molten filler metal and diffusion of filler metal elements to copper base metal. In recent times, thickness of copper base metals is reducing to lower the weight of products, therefore, in case of large erosion, molten filler metals penetrate through copper base metal resulting in the defects and degradation of joint quality and reliability. In the present work, the effect of filler metal composition of Cu-Sn-P and Cu-Ag-Sn-P alloys on the erosion depth of pure copper base metals was investigated using spread test specimens.

2. Experimental Procedures

Erosion depth of pure copper was measured at the center of the spread test specimen as shown in Fig. 1. The

size of the copper base metal was 40 × 40 × 1.1 mm, and the filler metal was 5 ϕ × 4 mm. The copper plate was JIS C 1020 oxygen free high conductivity copper. Precise experimental procedures of spread test are demonstrated in the previous paper⁵). Erosion depth was measured by a profile projector. The depth was coincided with the diffusion depth of filler metal elements such as tin, phosphorus and silver measured by energy dispersive analysis attached to a scanning electron microscope.

Microvickers hardness was also measured on filler metals of as cast condition and after spread test to examine the compatibility for practical use because the extremely hard materials would be brittle.

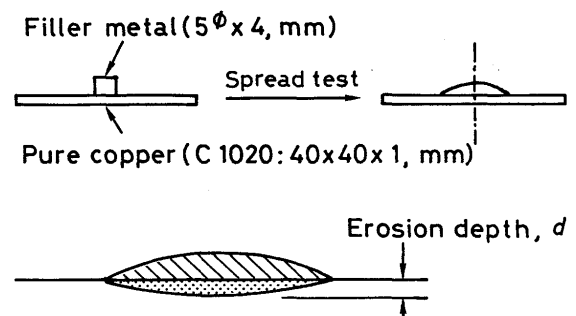


Fig. 1 Measurement of erosion depth at center of spread test specimen.

† Received on October 31, 1989

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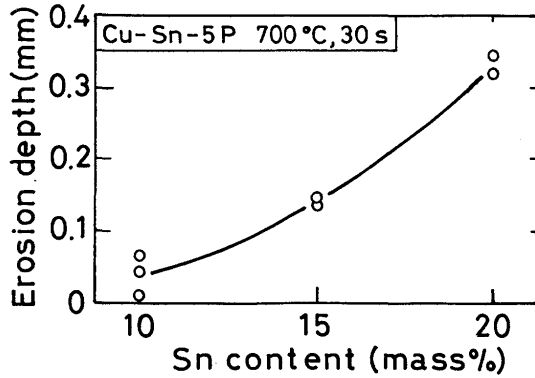


Fig. 2 Effect of tin content in Cu-Sn-5P filler metals on erosion depth of pure copper after spread test at 700°C for 30s.

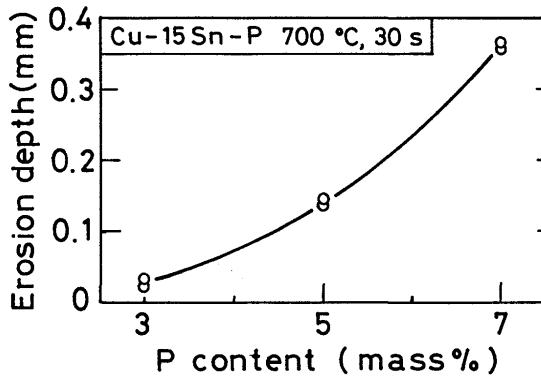


Fig. 3 Effect of phosphorus content in Cu-15Sn-P filler metals on erosion depth of pure copper after spread test at 700°C for 30s.

3. Results and Discussion

3.1 Ternary filler metals

Figure 2 shows the effect of tin content on the erosion depth of Cu-Sn-5P filler metals tested at 700°C for 30s. Increase of tin content enhanced erosion drastically. Similar effect was observed in phosphorus as shown in Fig. 3. Increasing the phosphorus content, erosion depth also increased. The erosion depth increased almost linearly with element content, however, Fig. 2 and 3 shows the relatively large increase at 7%P and 20%Sn that has Cu₃P primary phase, indicating the enhanced dissolution of pure copper as easily speculated by phase diagrams. Accordingly, the filler metals with primary copper solid solution, (Cu), or eutectic composition are recommended for practical use to lower the erosion of base metal.

Figure 2 and 3 revealed that the addition of tin and phosphorus enhanced erosion of base metal, therefore, the contents of these elements should be limited as low as possible considering the melting temperature range of filler metals.

Figure 4 shows the effect of holding time and

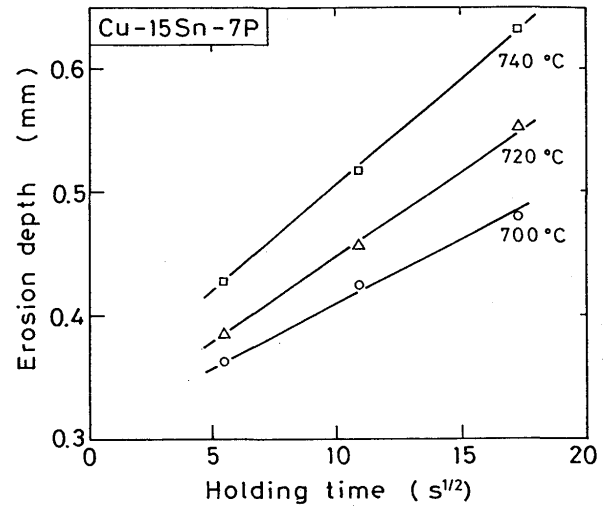


Fig. 4 Relation between erosion depth and square root of holding time at 700~740°C for Cu-15Sn-7P filler metals.

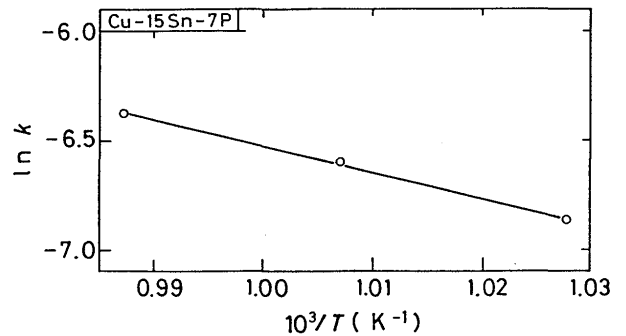


Fig. 5 Plots of ln k vs 1/T for Cu-15Sn-7P filler metals.

temperature on the erosion depth, d , for Cu-15Sn-7P filler metals. The erosion depth increased linearly with the square root of the holding time, \sqrt{t} . The results suggest that the erosion phenomena is controlled by the diffusion process. The extrapolation of the lines to $t=0$ exceeded 0 value of the erosion depth, this means that the erosion already proceeded during heating stage after initiation of melting of filler metals before reaching the holding temperature.

From Fig. 4, following equation holds between the erosion depth and the holding time,

$$d = k\sqrt{Dt} + A \quad (1)$$

where, k , A : constants, D : diffusion coefficient, and $D = D_0 \exp(-Q/RT)$, where, D_0 : constant, Q : activation energy, R : gas constant. Accordingly, the plots of erosion rate, k , vs. $1/T$ derives the activation energy for erosion reaction. The plots were put in a straight line as shown in Fig. 5.

The apparent activation energy of 195 kJ/mol is obtained. The value corresponded with the activation energy of diffusion of tin in solid copper, 188 kJ/mol⁷⁾, therefore, the erosion of this system might be controlled by the diffusion process of tin into copper base metal. In

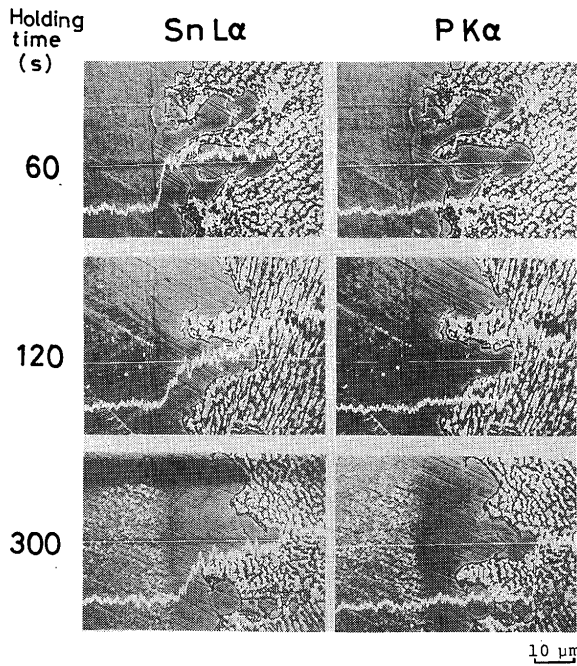


Fig. 6 Scanning electron micrographs and energy dispersive line analysis of Cu-15Sn-7P filler metal/base metal interface.

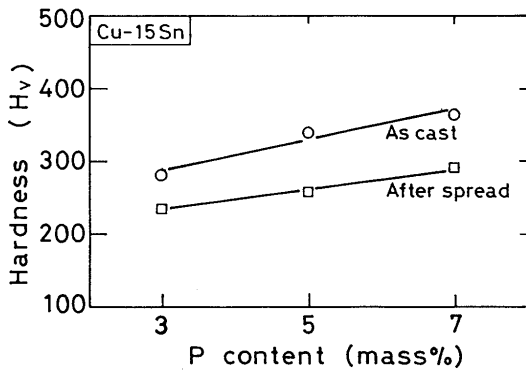


Fig. 7 Effect of phosphorus content on microvickers hardness of Cu-Sn-5P filler metals.

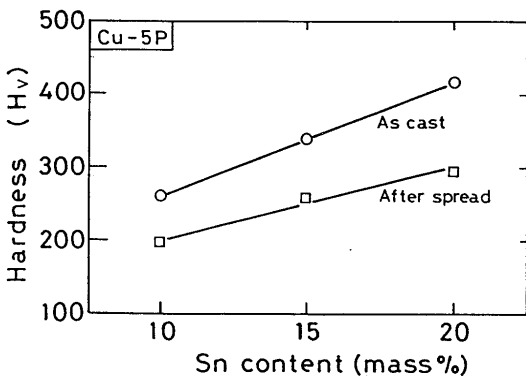


Fig. 8 Effect of tin content on microvickers hardness of Cu-Sn-5P filler metals.

fact the diffusion area of tin and phosphorus became broad with the holding time as shown in Fig. 6, cross section of base metal(left)/filler metal(right) interface.

Figures 7 and 8 show the change of hardness of filler

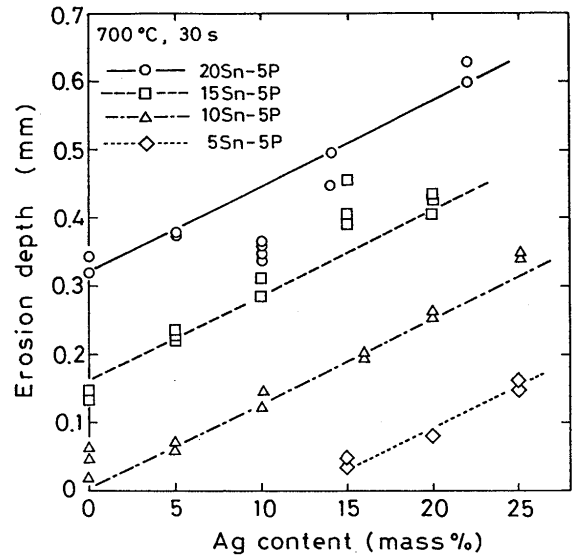


Fig. 9 Effect of silver and tin content in Cu-Ag-Sn-5P filler metals on erosion depth of pure copper after spread test at 700°C for 30s.

Table 1 Hardness increase per 1 mass% of each element in Cu-Sn-P brazing filler metals

Element	Hardness increase per 1 mass%	
	as cast	after spread
Tin	15.2	10.0
Phosphorus	20.8	13.8

metals with phosphorus and tin content respectively. In both figures, filler metals hardened almost linearly with phosphorus and tin content, because the addition of these elements increased the volume fraction of Cu_3P and/or $Cu_{41}Sn_{11}$ intermetallic compound phases with high hardness. Comparison of the hardness of as cast condition and after spread test revealed that the hardness was lowered after spread test especially in high phosphorus or tin filler metals with large erosion the remarkable softening was observed, thus the dissolution of copper into filler metals would be responsible to the low hardness after spread test.

The hardness increase per 1 mass% for tin and phosphorus was calculated as 15.2 and 20.8 respectively for cast filler metals and 10.0 and 13.8 for filler metals after spread test. The values are listed in Table 1.

3.2 Quaternary filler metals

Figure 9 shows the effect of silver and tin content on erosion depth of pure copper at 700°C for 60 s for Cu-Ag-Sn-5P filler metals. Erosion depth increased almost

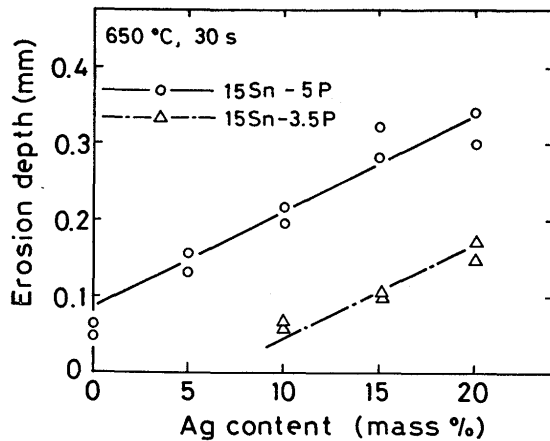


Fig. 10 Effect of silver and phosphorus content in Cu-Ag-15Sn-P filler metals on erosion depth of pure copper after spread test at 650°C for 30s.

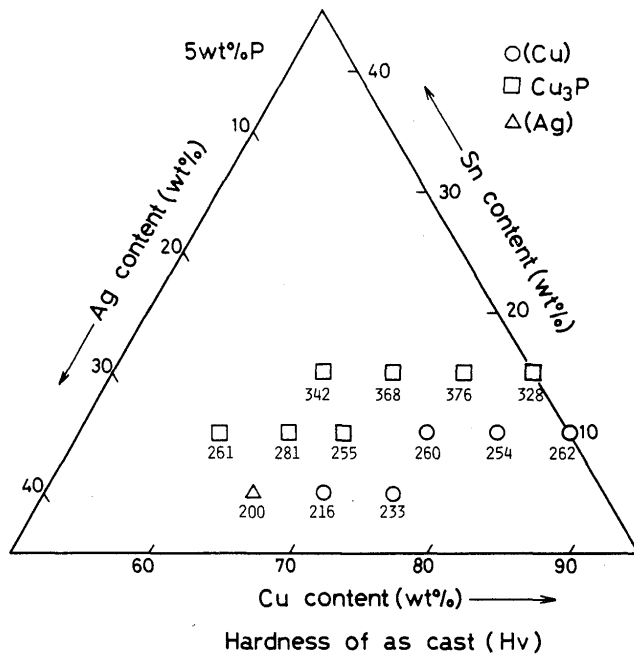


Fig. 11 Microvickers hardness of Cu-Ag-Sn-5P quaternary filler metals of as cast condition.

linearly with increasing silver and tin content. The erosion factor, increment of erosion depth of pure copper at 700°C for 30 s per 1 mass% of elements, were calculated as 0.032 and 0.013 for tin and silver respectively from the linear relations between element content and erosion depth in Fig. 9.

Figure 10 shows the effect of silver content in Cu-Ag-15Sn-3, 3.5P filler metals on the erosion depth at 650°C for 30 s. Similar to Fig. 9, erosion depth increased linearly with silver content. Increase of phosphorus also increased the erosion depth. Two lines are parallel in 3%P and 3.5%P, therefore, the erosion factor of phosphorus could be calculated by Figs. 9 and 10, 0.11 for 1 mass%P. The erosion factors are listed in **Table 2**.

From above results, erosion depth, d , could be

Table 2 Erosion factor of phosphorus, tin and silver in filler metals for pure copper base metals obtained at 700°C for 30s.

Elements	Erosion factor (mm/mass%)
Phosphorus	0.11
Tin	0.032
Silver	0.013

Table 3 Microvickers hardness of Cu-Ag-Sn-3.5P filler metals of as cast condition

Filler metals	Hv
Cu-25Ag-10Sn-3.5P	240
Cu-20Ag-10Sn-3.5P	238
Cu-20Ag-15Sn-3.5P	356
Cu-15Ag-15Sn-3.5P	382

expressed by the following experimental equations.

$$d = A \cdot M \cdot \exp(-Q/2RT)(\sqrt{t} + a) \quad (2)$$

$$M = 0.013[\%Ag] + 0.032[\%Sn] = 0.11[\%P] + b \quad (3)$$

where, A , a and b : constants, Q : activation energy = 195 kJ/mol, R : gas constant, T : test temperature(K), t : holding time(s). In the range of this experimental conditions, following values could be available: $A = 0.091$, $a = 5.6$, $b = -0.73$.

Figure 11 shows the microvickers hardness of Cu-Ag-Sn-5P quaternary filler metals of as cast condition. As well as the Figures 7 and 8, tin has the greatest influence on the hardness of filler metals, filler metals became drastically harder by increase of tin content. The hardness of quaternary filler metals with 3.5%P was summarized in **Table 3**. By decreasing the phosphorus content, hardness lowered, however, it is evident tin has more great influence on hardness under the same phosphorus content.

4. Conclusions

Measurement of the erosion depth of pure copper by molten copper phosphorus filler metals with tin and silver are summarized as follows.

- (1) Erosion depth increased linearly with holding time at 700 ~ 740°C. The activation energy of 195 kJ/mol were obtained for erosion reaction, the value was

well coincided with the activation energy for diffusion of tin in solid copper, therefore, the erosion reaction is suggested to be controlled by the diffusion of tin in solid copper base metal.

- (2) All filler metal elements such as phosphorus, tin and silver enhanced erosion. The erosion depth increased linearly with the amounts of elements in filler metals. The erosion factors for 1 mass% of each element are 0.11, 0.032 and 0.013 for phosphorus, tin and silver respectively, this is the descending order of the degree of enhancement for erosion.
- (3) Experimental equation for speculation of the erosion depth of pure copper by Cu-Ag-Sn-P filler metals was established.
- (4) Hardness of filler metal increased with amount of additional elements especially tin content, that increased the amount of intermetallic phase of Cu_3P and $\text{Cu}_{41}\text{Sn}_{11}$.

Acknowledgment

The authors would express their hearty thanks to Mr. S. Kawaguchi at Tanaka Precious Metals Col, Ltd. for presentation of noble metals.

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