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Spreading of Copper Phosphorus Brazing Filler Metals with Low Melting Temperature containing silver and/or Tin†

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

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

Abstract

Spreadability of copper phosphorus brazing filler metals with low melting temperature has been investigated on pure copper base metal. Spread tests were carried out between 650°C and 715°C in an air atmosphere without flux. Spread area of Cu-Sn-P filler metals were inferior to that of Cu-Ag-P filler metals, which is explained by the thermodynamic calculation that tin oxide is not so easily reduced by phosphorus compared with copper oxide. The spread area of Cu-Ag-Sn-P quaternary system filler metals were larger than Cu-Sn-P system at the same test temperature, however, the area was significantly smaller than in Cu-Ag-P ternary system. The fillet formation test in argon gas atmosphere revealed the good fillet was obtained in both Cu-Ag-P and tin bearing filler metals. Tin bearing filler metals showed better fillet appearance at lower brazing temperatures.

KEY WORDS : (Brazing filler metals) (Copper) (Spread test) (Silver) (Tin) (Copper phosphoprus alloys)

1. Introduction

Fluxless air atmospheric brazing of copper can be performed by using copper phosphorus brazing filler metals. Recently, the needs for the copper phosphorus brazing filler metals with low melting temperature becomes high. The addition of silver and tin has been proved to lower the melting temperature range of the filler metals [1,2] and some cross sectional phase diagrams have been established on Cu-Ag-P and Cu-Sn-P ternary alloys[3,4] and liquidus planes of ternary systems and Cu-Ag-Sn-P quaternary system[5,6], however, precise studies on the spread characteristics of the alloys with silver and/or tin has not been carried out yet sufficiently. Spreadability in an air atmosphere is one of the important factors for brazeability of copper phosphorus brazing filler metals, whether the alloy could be available for the practical use or not.

The aim of the present work is to clarify the spread characteristics of the copper phosphorus brazing filler metals with silver and/or tin addition.

2. Materials and Experimental Procedures

Spreadability were evaluated by the spread test on pure copper (oxygen free high conductivety copper) plate in an air atmosphere using Cu-Ag-P and Cu-Sn-P ternary alloys and Cu-Ag-Sn-P quaternary alloys. Shape and size of the specimens for spread test and fillet formation test are shown in **Fig. 1**. Copper base metal was polished with 600 grade emery paper and rinsed ultrasonically in an acetone bath prior to the test. The filler metal with a certain volume ($5^{\phi} \times 4$, mm) was put on the copper base metal. Spread test was carried out in an air atmosphere and fillet formation test was conducted in the argon gas flowing furnace shown in **Fig. 2**. Horizontally set copper base metal were heated by moving the pre-heated furnace and maintained at a predetermined temperature and

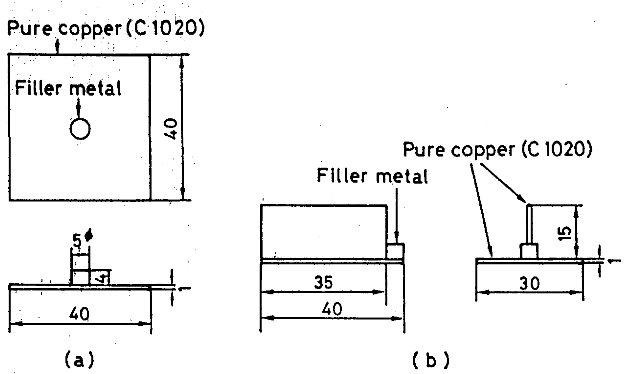

Fig. 1 Shape and size of brazing filler metal and pure copper base metal for spreading test (a), and for fillet formation test (b).

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cooled by removing the furnace. Spread area was measured by a projection projector.

Fillet formation test in an air and argon gas atmospohere were aslso conducted using specimens shown in Fig. 1(b). Specimens were set in a horizontal silica tube in which argon gas was flowing.

3. Results

3.1 Ternary alloys

Figure 3 shows the effect of phosphorus content in Cu-Ag-P filler metals on spread area tested at 670 and 700°C for 30 s. On the whole, the filler metals with 15%Ag showed larger spread area than filler metals with 10%Ag. Excellent spreadability was obtained in filler metals more than 7%P and Cu-15Ag-5P at 700°C. At 670°C, the spreadability was inferior to 700°C. In 10%Ag, primary phase planes of copper solid solution, (Cu), and Cu_3P cross at about 7.5%P[3,4], therefore the spread tests were carried out under liquidus in Cu-10Ag-7 and 8P filler metals. From the results of spread tests the amount of liquid at 670°C estimated to be larger in 7%P alloy than 8%P alloy, because the former alloy exihibited large spread area.

Figure 4 shows the spread area of Cu-Sn-P filler metals tested at 700°C for 30 s. In this system, specimens with spread area more tha 1cm^2 showed smooth and good spread appearance. Filler metals with 3%P and 7%Sn showed small spread area, however, in 4~7%P-15Sn and 5~7%P-10Sn filler metals larger spread area was obtained, showing that the addition of tin was proved to exert good spreadability of copper phosphorus brazing filler metals at 700°C. The decrease of spread area in Cu-15Sn~10Sn-7P filler metals would be attriblutable to the decrease of the amount of liquid phase at test temperature by the increased crystallization (liquidus) temperature of Cu_3P primary phase.

Figure 5 shows the changes of spread area of Cu-15Sn-5P alloy during holding at 685~715°C. Filler metal gradually spread on base metal up to holding time 300 s. At 685°C, spread area was significantly increased by holding 30~120 s, after that spread area was unchanged. On the whole, holding time has a little effect on spread area.

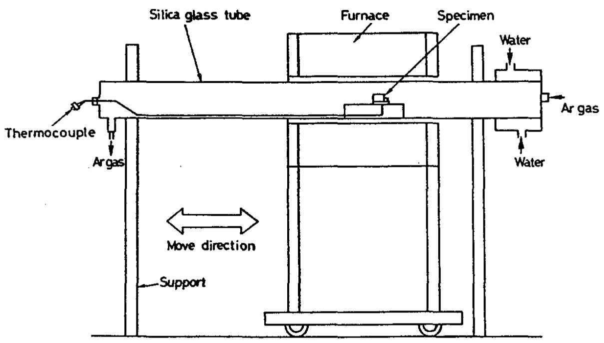

Fig. 2 Illustration of apparatus for fillet formation test in argon gas atmosphere.

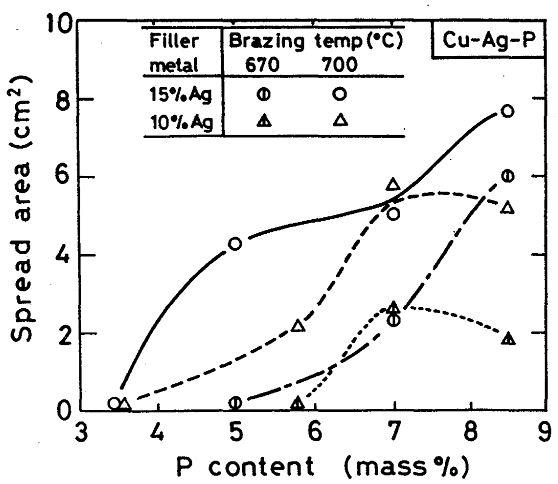

Fig. 3 Spread area of Cu-Ag-P filler metals on copper base metal at 670 and 700°C for 30 s.

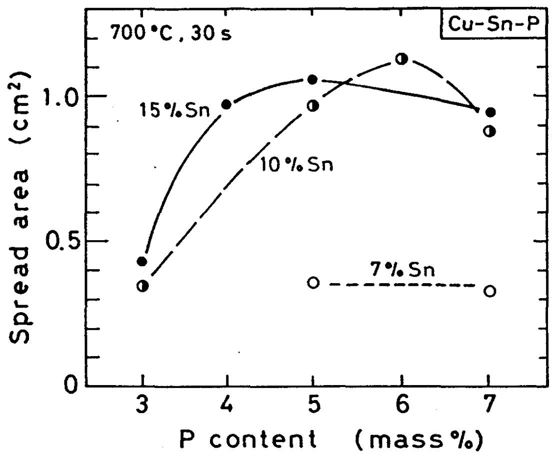

Fig. 4 Spread area of Cu-Sn-P filler metals on copper base metal at 700°C for 30 s.

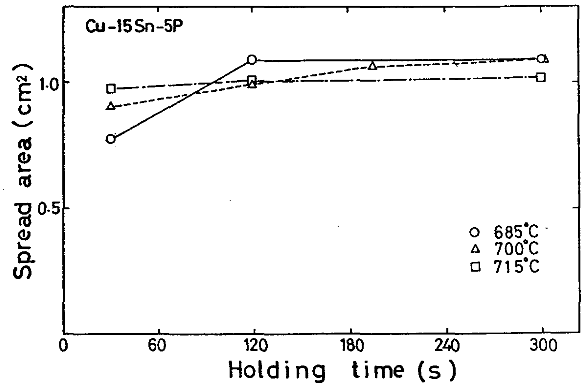

Fig. 5 Effect of holding time at 685~715 °C on spread area of Cu-15Sn-5P filler metal.

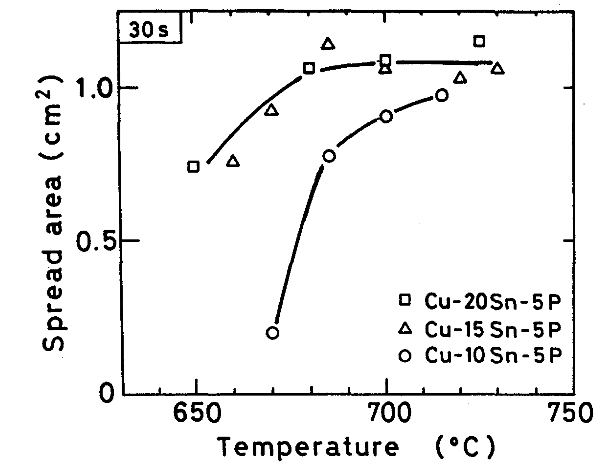

Fig. 6 Effect of test temperature on spread area of Cu-10 ~ 20Sn-5P filler metals at 650~730°C for 30 s.

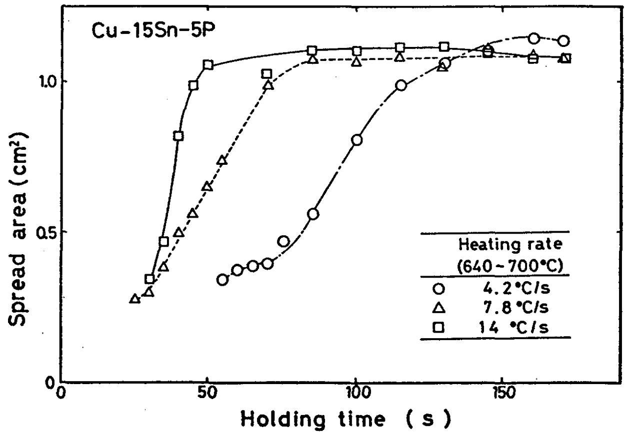

Fig. 7 Changes of spread area during heating stage under different heating rate.

Figure 6 shows the effect of temperature on spread area of Cu-10~20Sn-5P filler metals. Spread area corresponded to their melting point (liquidus temperature), Cu-10Sn-5P filler metals, liquidus is about 750°C[3,4], scarcely spread at 670°C and even at 700°C the spread area was smaller than tin rich filler metals. Cu-15 and 20Sn-5P filler metals, the liquidus temperatures are 706°C and 625°C respectively[3,4], exhibited larger spread area at lower temperature.

Figure 7 shows the changes of spread area during heating stage of Cu-15Sn-5P filler metal under different heating rate. Of cource, large spread area was obtained under high heating rate at short heating time, however, after 150 s almost the same spread area was obsreved irrepective of heating rate.

Figure 8 is the plots of spread area vs. temperature. Under high heating rate, spread area was small at temperature below 700°C, however, almost the same spread area was observed at more than 700°C. The difference in spread area under 700°C would be attritbutable that the temperature of filler metal might

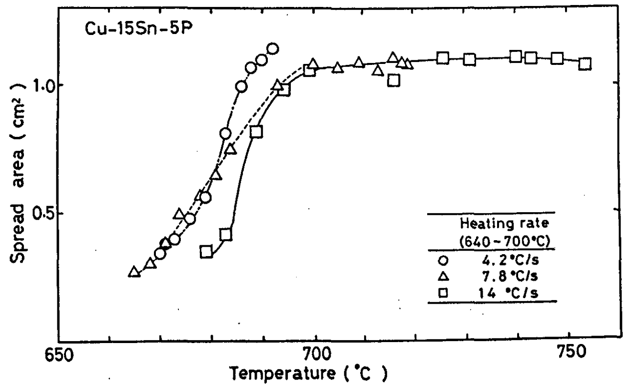

Fig. 8 Plots of spread area vs. base metal temperature for different heating rate.

significantly lower than base metal under high heating rate.

3.2 Quaternary alloys

Figure 9 and **10** show the spread area of Cu-Ag-Sn-5P filler metals on copper plate at 700°C and 650°C for 30 s respectively. In this system, similar to Cu-Sn-P ternary system, specimens with spread area of more than 1 cm^2 showed smooth and good spread appearance. Large spread area was obtained at higher temperature, 700°C, however, the similar dependence on filler metal composition was obtained at both temperatures, Cu-10~20Ag-15~20Sn-5P filler metals showed good spreadability. In 5%Sn filler metal, only poor spreadability was observed due to the small amount of liquid at test temperatures, because the filler metal has relatively higher liquidus temperatures[5,6].

4. Discussions

Tin addition to copper phosphorus brazing filler metals lowered the liquidus temperature and enhanced the low temperature brazeability, however, the spreadability of tin bearing filler metals was remarkably smaller than Cu-Ag-P filler metals especially at 700°C.

The free energies of oxide formation reactions as $2Ag + 1/2O_2 = Ag_2O$, $4Cu + O_2 = Cu_2O$, $Sn + O_2 = SnO_2$, $2/5P_2 + O_2 = 2/5P_2O_5$, were about + 32, − 209, − 385, − 410 kJ/mol respectively[7,8]. The value of free energies indicate that the tin oxide is more stable than silver and copper oxides. The value for tin are slightly larger than phosphorus thererfore, tin oxide would be more difficult to be reduced by phosphorus than copper oxide. Silver oxide, Ag_2O, dissolves into silver and oxygen at 700°C[9], therefore, the following discussions examine the reductioin reaction whether the tin oxide is reduced by phosphorus. Here, the values of tin is used as liquid state considering tin in molten filler metal[10]. The phases of liquid, gas and solid are represented as (*l*), (*g*) and (*s*)

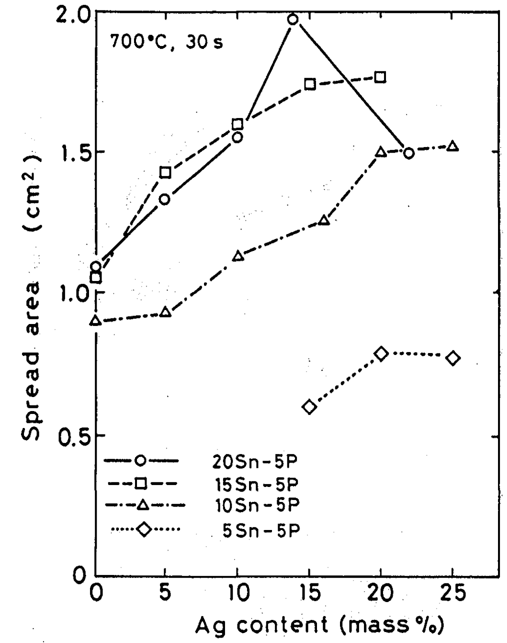

Fig. 9 Spread area of Cu-Ag-Sn-5P quaternary filler metals on copper base metal at 700°C for 30 s.

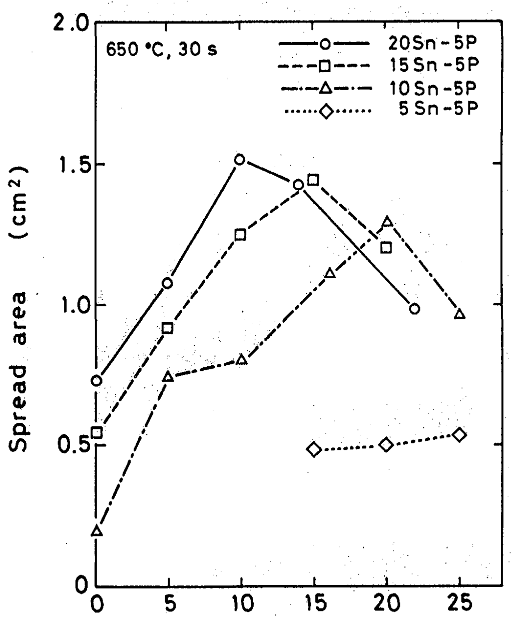

Fig. 10 Spread area of Cu-Ag-Sn-5P quaternary filler metals on copper base metal at 650°C for 30 s.

Table 1 Vertical leg length, L_V, horizontal leg length, L_H, and leg length ratio, L_V/L_H formed by fillet fomation test in argon gas

Filler metals	Fillet formation test temperature (℃)	L_V (mm)	L_H (mm)	L_V/L_H
Cu-15Sn-5P	685	2.92	2.18	0.747
Cu-10Ag-7P	700	2.15	1.65	0.766
Cu-16Ag-10Sn-5P	685	2.05	1.55	0.755
Cu-15Ag-15Sn-3.5P	650	1.98	1.40	0.709
Cu-20Ag-15Sn-3.5P	650	2.18	1.59	0.730
Cu-15Ag-15Sn-4P	650	2.06	1.52	0.740

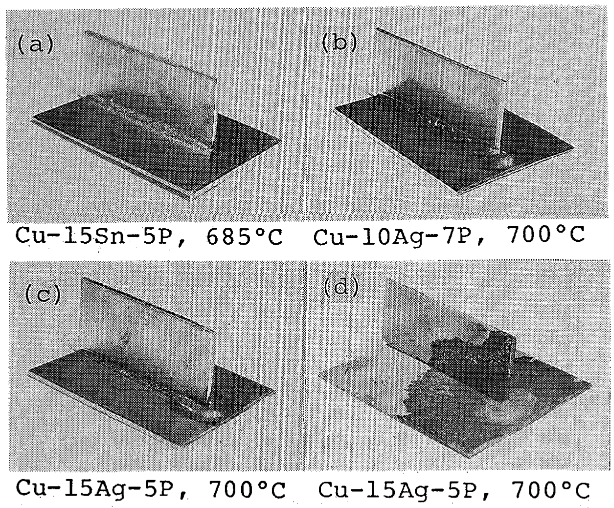

Fig. 11 Appearance of specimens after fillet formation test in an air and argon gas atmospheres, (a)~(c): argon gas, (d): air.

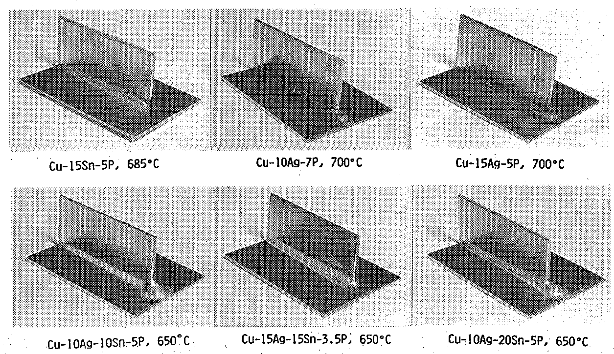

Fig. 12 Appearance of specimens after fillet formation test in an air and argon gas atmosphere.

respectively.

$$Sn(l)+O_2(g)=SnO_2(s) \quad (1)$$
$$\Delta G^\circ=-135{,}500+47.15T$$
$$Sn(l)+1/2O_2(g)=SnO(s) \quad (2)$$
$$\Delta G^\circ=-67{,}600+24.64T$$
$$1/2P_2(g)+1/2O_2(g)=PO(g) \quad (3)$$
$$\Delta G^\circ=-27{,}000+2.28T$$
$$2P_2(g)+5O_2(g)=P_4O_{10}(g)$$
$$\Delta G^\circ=-750{,}000+230.6T$$

From eqs. (1) and (3),

$$P_2(g)+SnO_2(s)=Sn(l)+2PO(g) \quad (5)$$
$$\Delta G^\circ=81{,}500-42.59T \quad (5)'$$

From eqs. (2) and (3),

$$1/2P_2(g)+SnO(s)=Sn(l)+PO(g) \quad (6)$$
$$\Delta G^\circ=40{,}600-22.36T \quad (6)'$$

From eqs. (1) and (4),

$$2P_2(g)+5SnO_2(s)=Sn(l)+P_4O_{10}(g) \quad (7)$$
$$\Delta G^\circ=-73{,}200-5.15T \quad (7)'$$

From eqs. (2) and (4),

$$2P_2(g)+10SnO(s)=10Sn(1)+P_4O_{10}(g) \quad (8)$$
$$\Delta G^\circ=-74{,}700-15.8T \quad (8)'$$

By putting 700°C(973K) into eqs. (5)' ~ (8)', the following values of +168, +78.7, −327 and −377 kJ/mol are obtained respectively, indicating that the reactions of eqs. (5) and (6) are difficult to occur, however, the reactions of eqs. (7) and (8) are possible, therefore, it is found that the tin oxide can be reduced by phosphorus. Similar calculations were conducted on liquid copper and oxygen for both copper oxides as CuO and Cu_2O. The all free energies of the reduction reactions of copper oxides by phosphorus showed that the reduction of copper oxide is more easy than tin oxide. Above caluculations indicate that the surfacre oxide film on Cu-Sn-P filler metals is more stable than Cu-Ag-P filler metals, which is the one reason of the small spread area in Cu-Sn-P filler metals.

Even the tin bearing filler metals have lower melting points than Cu-Ag-P filler metals showed inferior spreadability because tin oxide is more difficult to be reduced by phosphorus. Fillet formation tests were conducted in an air and argon gas atmosphere. The appearances of specimens after fillet formation test are shown in **Fig. 11** for ternary filler metals. In air atmosphere, no fillet was obtained in both Cu-Ag-P and Cu-Sn-P filler metals as shown in Fig. 11(d). In argon gas atmosphere Cu-15Sn-5P filler metal formed excellent fillet at 685°C, however, Cu-10Ag-7P and Cu-15Ag-5P filler metals showed the solid phase remained at the set position still unmelted even at 700°C, indicating the typical liquation phenomina.

Figure 12 shows the appearance of specimens after fillet formation test in argon gas atmosphere at 650 or 685°C for quaternary filler metals. Specimens with the lowest melting point, Cu-20Ag-15Sn-3.5P filler metal, showed the best fillet form at 650°C.

Table 1 shows the leg length and leg legth ratio, L_V/L_H, L_V: vertical leg length, L_H: horizontal leg length for the fillets formed in argon gas atmosphere. As mentiioned above, all specimens showed sound fillet in argon gas atmosophere.

Cu-20Ag-15Sn-3.5P filler metal had large fillet. The leg length ratio over 0.7 was obtained indicating relatively good fillet. The fillet formation test revealed that the test in non-oxidizing atmosphere in argon gas gave sound fillet in tin bearing filler metals.

5. Conclusions

The results obtained by the spread test of copper phosphorus brazing filler metals on pure copper in an air and argon gas atmosphere were summarized as follows.

(1) Tin bearing filler metls showed inferior spreadability to Cu-Ag-P ternary filler metals under the same test conditions.

(2) Thermodynamic calculations on the reduction reaction by phosphorus revealed that copper oxide is more easily reduced by phosphorus compared to tin oxide.

(3) Quaternaty filler metals with lower melting temperatures showed better spread area than Cu-Sn-P filler metals, and the quaternary alloys could be usable at 650°C.

(4) The tin bearing filler metals with lower melting points, however, showed good fillet formability in protection atmosphere at lower temperatures.

Acknowlegement

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