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Copper Phosphorus Brazing Filler Alloys with Low Melting Temperature (Report I)†
– Effect of Tin Addition –

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Abstract

A new copper phosphorus self-fluxing filler alloy applicable to brazing at 650°C has been developed by the addition of tin to Cu-Ag-P alloy. The influence of tin, phosphorus and silver content on the brazability at 650°C has been investigated by evaluating the penetration length of filler alloy between two copper plates of 0.1 mm lap joint clearance. Differential thermal analysis and metallographic observation were also carried out to define the temperature ranges of melting and the phase changes. Whthin the range of this investigation, the availabe filler alloy composition was found to be Ag/Cu (15/65)-15%Sn-(3 ~ 3.5)%P. The solidus and liquidus temperatures of the alloys were about 475°C and 620 ~ 650°C, respectively. The alloys of more than 3.5%P content having primary Cu_3P phase showed poor penetration length because phosphorus content in coexisting liquid decreased due to the formation of Cu_3P. On the other hand, the alloys of less than 3.5%P content crystallized primary α-Cu phase, and then the coexisting liquid contained more phosphorus than the nominal concentration. Accordingly, the alloys exhibited excellent fluxing action.

KEY WORDS: (Brazing) (Brazing Metal) (Copper Alloys) (Low) (Melting Point)

1. Introduction

Fluxless brazing of copper in air atmosphere has been performed by use of copper-phosphorus brazing filler alloys. Five self-fluxing copper-phosphorus brazing filler alloys have been given in the JIS specification Z 3264, and widely used for brazing copper where residues of corrosive fluxes should be avoided. The solidus temperature ranges of commercial copper-phosphorus brazing alloys are about 640 ~ 705°C[1]. Step brazing of copper without fluxes has been carried out by first brazing operation with BCuP-1 followed by brazing with BCuP-3 ~ 5. But filler alloy with lower melting temperature is preferable from a point of view of prevention of degradation of base metal and simple brazing operation. Furthermore, known modified copper-phosphorus filler alloys with low melting temperature could not reward the need for following third brazing operation after brazing by BCuP-5[2) 3)]. The objective of this study was to develop a new copper-phosphorus filler alloys with low melting temperature which can be used for second brazing operation on BCuP-5 brazed copper joint.

2. Determination of the brazing temperature for a new filler alloy

At the first stage of development of the new copper-phosphorus filler alloy, the appropriate operation temperature of the filler alloy should be chosen under consideration of the step brazing with BCuP-5. A new filler alloy should be able to be used below the remelting temperature of a copper lap joint brazed by BCuP-5. To determine the appropriate operation temperature, a copper lap joint brazed with BCuP-5 was put into a furnace at 900°C and the temperature at which the lower copper plate dropped was measured as a function of the lap clearance. Copper plates ($20^w \times 70^l \times 5^t$, mm) with 7 mm lap length and clearances of 0 (not intensionally pressed) to 1.7 mm were brazed in air by a torch at 750°C for 30 sec without flux. **Figure 1 (a)** shows an illustration of the drop test method to detemine the drop temperature which was measured by a thermocouple attached to the hanged specimen. Figure-1 (b) shows the relationship between remelting temperatures and clearances of copper lap joints brazed with BCuP-5. Under the condition where clearance of more than 0.5 mm, the lower copper plates dropped off at 675°C, about 30°C higher than the solidus temperature of

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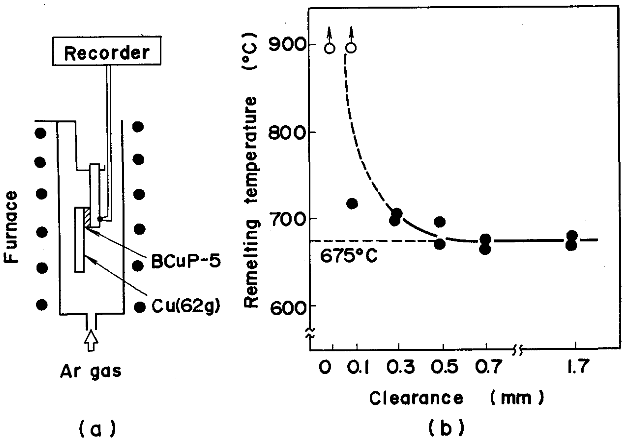

Fig. 1 Illustration of testing method for determination of remelting temperature (a), and remelting temperature of copper lap joints brazed by BCuP-5 with various clearances (b)

BCup-5. But in the joints within 0.1 mm clearances, the lower pieces did not drop off even heated up to 900°C, which was higher than the nominal liquidus temperature (802°C). The results indicate that the copper base plate was dissolved into the molten filler alloy so much that the remelting temperature of brazed joint was raised to some extent. From the results shown in Fig. 1(b) the appropriate operation temperature of a new filler alloy for the second brazing step of a BCuP-5 brazed copper joint was evaluated to be about 650°C.

3. Materials and experimental procedures

Copper-phosphorus alloys were made from Cu-15%P alloy, 99.99% electric copper and high purity silver and tin. The compounded materials were put in a graphite crucible and heated in argon atmospher sturring by a graphite rod and cast at 900°C into an iron mold of 5 mm diameter. Commercial BCuP-5 of 2.4 mm diameter was also used as a reference filler material.

To evaluate the applicability for brazing at 650°C, a penetration test between copper plates was adopted. **Figure 2** shows the shape and size of the penetration test specimen. Copper plates ($30^w \times 40^l \times 1^t$, mm) were polished by 600 grade emery paper and then rinsed in an ultrasonic acetone bath. To maintain the clearance of 0.1 mm, molybdenum wires ($3^l \times 0.1^\phi$, mm) were set between copper as shown in Fig. 2 (a). Two copper plates with 24 mm lap length were set horizontaly in a quartz tube. The filler alloy and a rectangular stainless steel weight ($15^w \times 25^l \times 8^t$, mm) were put on the copper plates not to allow the upper plate to move during melting of filler alloy. Then a preheated electric furance was set to cover the quartz in an air atmosphere. Heating rate was

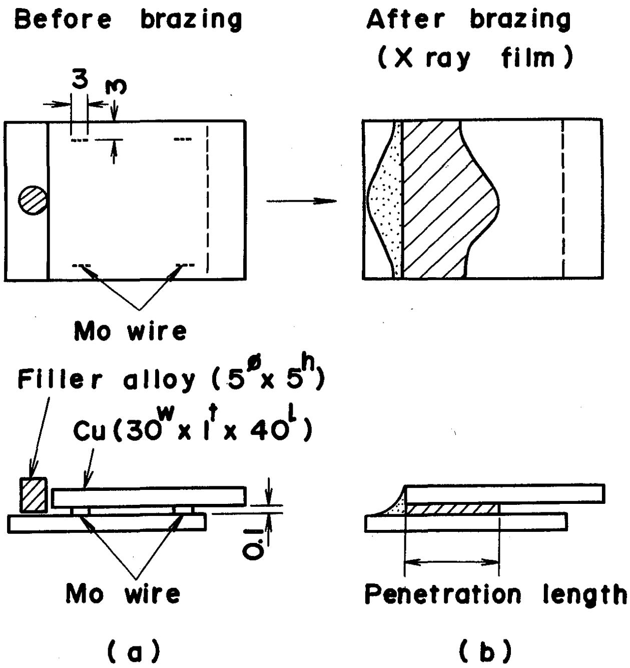

Fig. 2 Shape and size of penetration test specimen (a) and definition of penetration length (b)

about 100°C/min. After the temperature of specimen reached 650°C, the furnace was removed and specimen was air cooled. After this brazing process, the maximum penetration length of molten filler alloy into copper plates was investigated by a measurement of transmission X-ray photographs (75 kV, 12 mA). Other parameters such as penetration area and the penetration length at edge of lap specimen were also measured. Liquidus and solidus temperatures of laboratory made copper-phosphorus alloy were measured by means of differential thermal analysis (DTA) during cooling stage. Sample for DTA was put in a quartz tube and heated up to about 750°C and cooled in an air atmosphere. Cooling rate eas about 4°C/min. Vacuum sealed copper powder was used as the standard sample.

4. Results and discussions

4.1 Effect of tin addition

Tin addition up to 10% has been applied to lower the melting temperature of BCuP filler alloys. Ag-Cu-Sn ternary diagram[4] shows that 15Ag-65Cu-20Sn (wt %) alloy has a liquidus temperature of 770°C. To exert self-fluxing ability upon brazing, addition of phosphorus is essentiol and it also provides low melting temperature to Cu-Ag-Sn alloys.

Figure 3 shows the results of differential thermal analysis (DTA) on Cu-15Ag-5P (BCuP-5) and Cu-15Ag-5P-15Sn

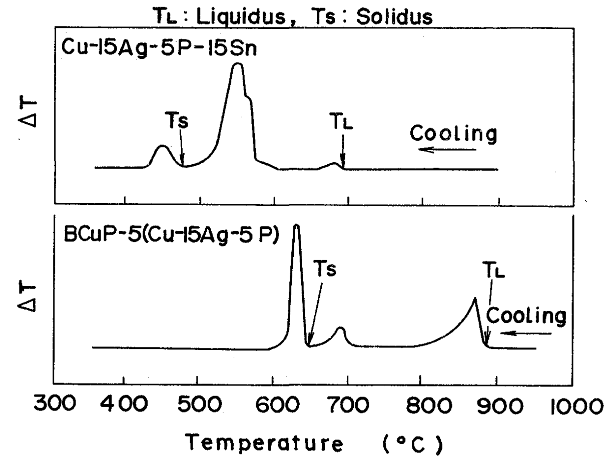

Fig. 3 DTA curves of copper phosphorus brazing filler alloys during cooling stages

alloys. BCuP-5 crystalized at 883°C yielding primary α-Cu phase, and then α-Ag phase appeared at 701°C, and finaly it solidified at 644°C by ternary eutectic reaction. The recommended brazing temperature ranges of the JIS specification are approximately the temperatures between the liquidus and peritectic temperatures. The measured liquidus temperature of BCuP-5 is higher than the reference value in the JIS. This difference can be explained in terms of phosphorus content which greatly influences the liquidus temperature because the standard value allows of fairly wide phosphorus composition range of 4.8 $\sim$ 5.3%.

On the other hand, the liquidus temperature of laboratory made Cu-15Ag-5P-15Sn alloy was 686°C and the solidus one was 469°C, which indicated a possibility that a new filler alloy capable of brazing at 650°C could be developed by tin addition through appropriate selection of composition.

Then the next stage of examination involved effects of tin addition on microstructure, penetration length and melting temperature. **Figure 4** shows the microstructure of cast filler alloy with 10 $\sim$ 25%Sn. The filler alloy composition was varied under such condition that the ratio of silver content to copper content is always 15/65. Dendritic bright phase was Cu_3P, which was confirmed by X-ray diffractometer (CuKα, Ni filter, 35kV, 10mA), black phase was α-Cu solid solution containing tin and phosphorus, and fine eutectic structure was composed of α-Ag, α-Cu and Cu_3P and moreover Cu-Sn intermetallic compound was also found in some tin rich alloys. Primary phase of these alloy was found to be Cu_3P by microscopic observations on the specimens quenched from the temperature between liquidus and subsequent reaction. As tin

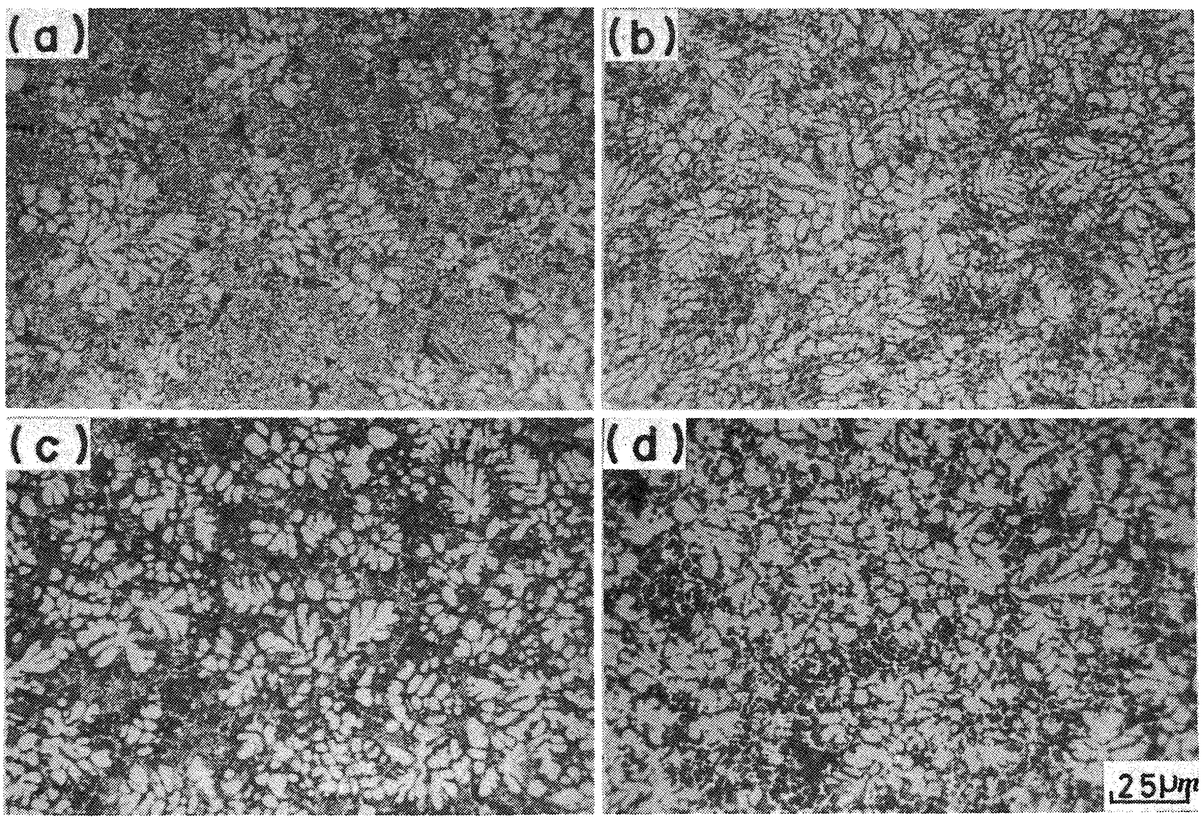

Fig. 4 Microstructure of loboratory cast filler alloys of various tin content
(a) 10%Sn, (b) 15%Sn, (c) 20%Sn, (d) 25%Sn

content was increased, the amount of primary Cu_3P phase increased as clearly shown in Fig. 4.

Figure 5 indicates the effect of tin content on penetration length at 650°C in air without flux. The other parameters such as penetration length at edge of specimen also showed similar relationships. Penetration length of 10%Sn alloy was less than 5 mm, and the length increased to some extent in 15 ~ 25%Sn alloys, however, the irreproducibility of penetration length provided fairly large scattering. At 650°C, BCuP-5 did not penetrate between two copper plates, but remained at the placed position showing partially melted form. At this temperature, laboratory made filler alloy consisted of primary Cu_3P and liquid, while BCuP-5 showed solid phases (α-Cu+α-Ag +Cu_3P) and liquid. The amount of liquid was extremely small in BCuP-5 at 650°C.

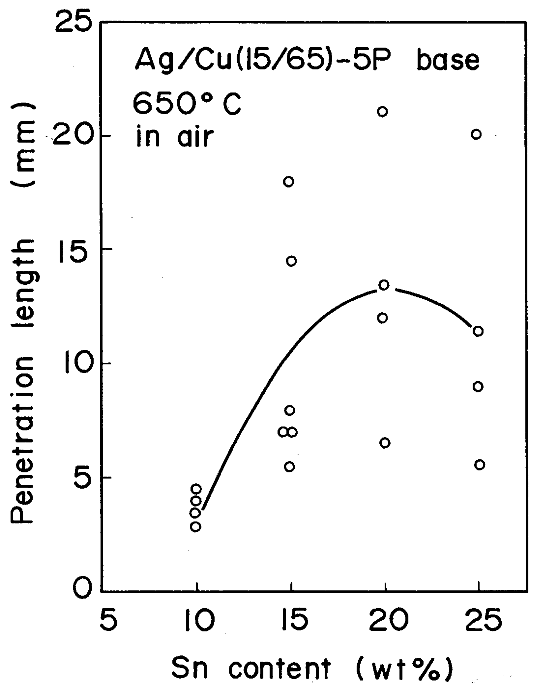

Fig. 5 Effect of tin content on penetration length of Ag/Cu(15/65)-5P base filler alloys

Figure 6 represents the results of the spread test at 650°C for 30 sec on horizontal copper plates by use of disk-shaped Ag/Cu(15/65)-5P base alloys ($5^{\phi} \times 3^{h}$, mm). The 15 ~ 20%Sn alloys produced large spread area in agreement with the results of the penetration test. The above mentioned results demonstrates that the proper tin content appears to be about 15%.

4.2 Effect of phosphorus content

Figure 7 shows the liquidus and solidus temperatures of Ag/Cu(15/65)-15%Sn-3 ~ 7%P alloys. The liquidus temperature ran through a minimum at about 3.5%P with

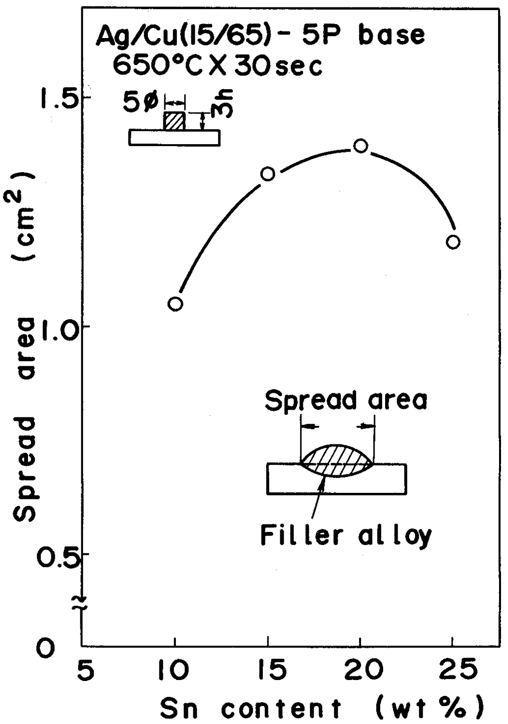

Fig. 6 Relation between spread area and tin content

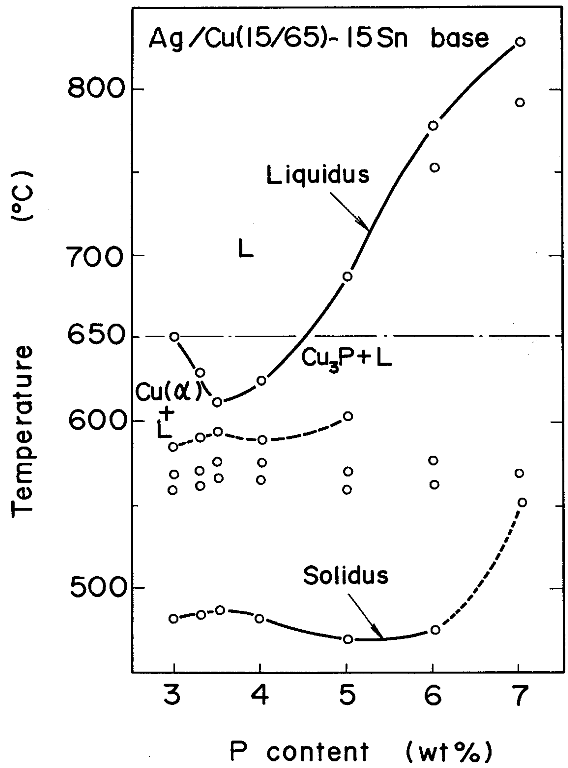

Fig. 7 Result of DTA of various phosphorus content copper phosphorus filler alloys

increasing phosphorus content, however, it rose with phosphorus content up to 7%. The alloys with less than 3.5%P showed primary α-Cu phase and the ones with 4 ~ 7%P exhibited primary Cu_3P phase. Solidus line showed no remarkable changes in 3 ~ 6%P alloys, but it seemed to increase to 550°C in 7%P alloy in accordance with the microscopic observation which showed no quaternary eutectic reaction. The broken line under liquidus indicates the binary eutectic and the other reactions which involeves the crystalization of Cu_3P. The open circles between liquidus and solidus in Fig. 7 shows eutectic and other reactions but this paper will not include the identification of each reaction. **Figure 8** shows the microstructure of cast alloys with 3~7%P. Black primary α-Cu phase is observed in 3%P alloy, while bright dendritic primary Cu_3P phase is observed in 4 ~ 7%P alloys. In 3.5%P alloy, only fine microstructure like eutectic is observed. The amount and size of primary Cu_3P phase increased with increasing phosphorus content.

Figure 9 shows the penetration length of various phosphorus content filler alloys between copper plates. Relatively large irreproducibility in penetration length like Fig. 5 is also shown. The irreproducibility is rather large in alloys with 5 ~ 7%P because the alloys contain Cu_3P

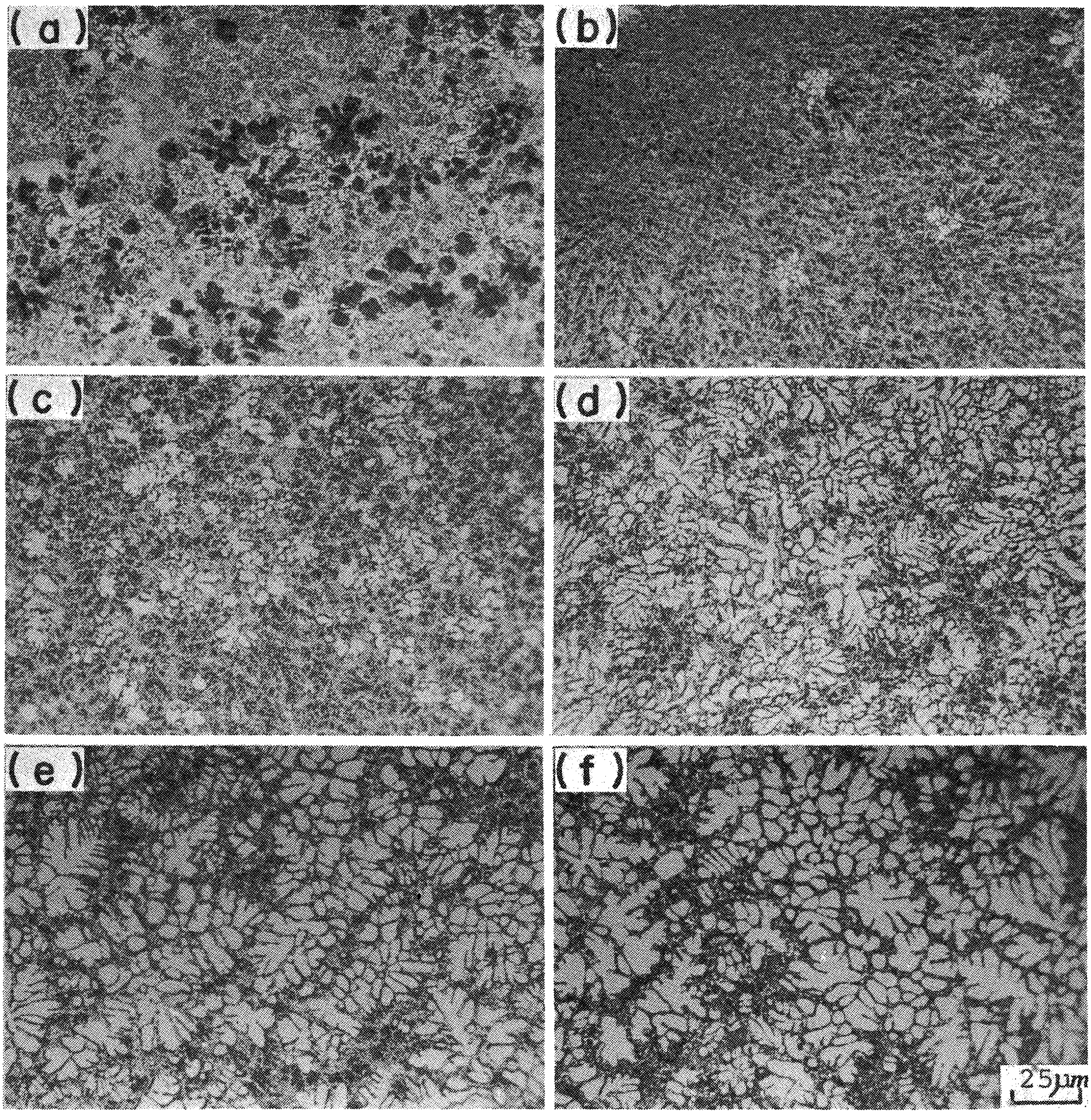

Fig. 8 Microstructure of laboratory cast filler alloys of various phosphorus content
(a) 3%P, (b) 3.5%P, (c) 4%P, (d) 5%P, (e) 6%P, (f) 7%P

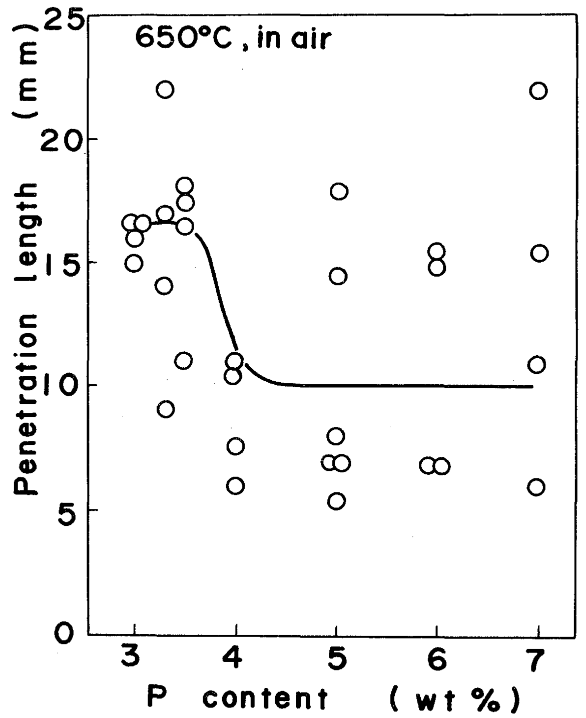

Fig. 9 Penetration length of various phosphorus content Cu/Ag-(15/65)-15Sn base filler alloys

primary phase at test temperature of 650°C. Althougth, scattering is also observed in alloys with low phosphorus content except 3%P alloy. The reason may be attributed to the coexistence of various solid phases during heating up to brazing temperature. Narrow scattering range of 3%P alloy seemed to be related to the decrease in erosion depth as the crystalized amount of primary α-Cu phase increased with decreasing phosphorus content. As alloy with 7%P had considerably much primary Cu_3P phase, unmelted Cu_3P phase remained at its preplaced position even the specimen showed good penetration characteristics. Consequently, the alloy much phosphorus content was not suitable for brazing fillers. From the results shown in Fig. 9 and the avobe mentioned facts, the alloys with 3 ~ 3.5%P are recommended for brazing at 650°C. These alloys completely become homogeneous liquid at 650°C. And the alloy with 4%P was also able to become homogeneous liquid, however, the penetration length was slightly short. The alloy with 4%P has liquid and Cu_3P, while the alloys with 3 ~ 3.5%P have liquid and α-Cu phase between liquidus and broken line shown in Fig. 7. The recommended brazing temperatures given in the JIS are approximately the coexisting temperatures of liquid and α-Cu phase. The amount of dissolved phosphorus in liquid coexisting with Cu_3P phase is lower than the gross concentration of phosphorus because phosphorus content in Cu_3P phase is higher than the gross composition. Therefore, the effective self-fluxing action is reduced. On the other hand, the liquid coexisting with α-Cu phase contains more dissolved phosphorus than the gross values as phosphorus in α-Cu phase is less than the gross ones. Thus the alloys with α-Cu phase and liquid seem to be able to exert active self-fluxing reaction during brazing of copper. The 4%P alloy becomes homogeneous liquid during heating to 650°C, but the penetration length was short. Following reasons are expected to explain the short penetration length of 4%P alloy. The 4%P alloy contains primary Cu_3P phase under liquidus temperature, it takes several moments that primary Cu_3P dissolves into liquid, and unmelted Cu_3P phase may remain in the liquid filler metal penetrated into narrow gaps due to heterogeneous liquation. The retained Cu_3P can act as an obstacle to penetrating liquid into gaps. As the broken line shown in Fig. 7 indicates eutectic and the other reactions, whole solid phases except primary phase liquate above this temperature. The working temperature 650°C is 50°C higher than the melting temperature of eutectic Cu_3P phase in 3 ~ 3.5%P alloys, which showed good penetration characteristics. The melting temperatures of Cu_3P in the alloy with more than 4%P, which has primary Cu_3P, are liquidus temperatures, and the difference in temperature between 650°C and liquidus is less than 50°C. From these results, the recommended operation temperature of filler alloy was found to be at least 50°C higher than the melting temperature of eutectic Cu_3P, and moreover the appropriate composition ranges of filler alloy is to be selected under the condition that the alloy has not primary Cu_3P phase but primary α-Cu phase.

4.3 Effect of silver content

The above mentioned results indicated that Ag/Cu/(15/65)-15Sn-3 ~ 3.5P alloy could be used at 650°C as a low melting temperature copper-phosphorus brazing filler alloy. The object of silver addition to copper-phosphorus alloy was to provide low melting temperature, therefore, appropriate content of silver and tin was investigated. Silver contents were varied within the range of 10 ~ 22%. **Figure 10** represents the effect of silver content on penetration length using Cu-15Sn-3.5P and Cu-15Sn-5P base alloys. Penetration length increased with increasing silver content in Cu-15Sn-5P base alloy, however, 15%Ag alloy exhibited maximum penetration length in Cu-15Sn-3.5P base alloy. The other examination on alloys with equivalent silver and tin content of 10 ~ 15% revealed that no alloys apperared to be superior to the alloys shown in Fig. 10 from a point of view of penetration length and erosion of base plate. The results of DTA on these alloys revealed that the liquidus temperature of alloys with

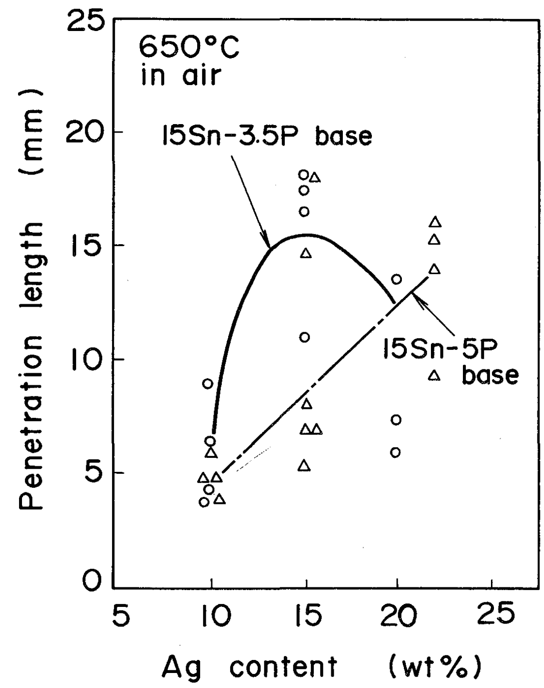

Fig. 10 Effect of silver content on penetration length

much silver content was relatively low, however, phosphorus and tin content also related to the melting temperatures. Accordingly the relations between filler alloy composition and melting temperature range were very complicated. After all, the most suitable composition for Cu-Ag-Sn-P system low melting point brazing filler alloy was found to be Ag/Cu(15/65)-15Sn-3 ~ 3.5P.

5. Conclusions

A new copper phosphorus brazing filler alloy with low melting temperature applicable to second step brazing process for BCuP-5 brazed copper joint has been developed in terms of tin, phosphorus and silver content. Addition of tin to Cu-Ag-P alloy was effective to lower both liquidus and solidus, and a new filler alloy for brazing at 650°C was developed by a series of selections of filler alloy composition. The brazability of filler alloy was evaluated by penetration length of melted filler alloy into copper lap joint with 0.1 mm clearance. The obtained results are summarized as follows.

(1) The primary phase in solidification differed with phosphorus content in Ag/Cu-15Sn alloys. The alloys with less than 3.5%P exhibited primary α-Cu solid solution, but the alloys with more than 4%P provided primary Cu_3P phase. The solidus temperatures of 3 ~ 6%P alloys were about 460 ~ 470°C.

(2) The penetration lengths of 3 ~ 3.5%P alloys with primary α-Cu phase were superior to those of 4 ~ 7%P alloys with Cu_3P primary phase.

(3) Over the range of this investigation, the most suitable composition of filler alloy for brazing at 650°C was found to be Ag/Cu(15/65)-5Sn-3 ~ 3.5P.

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