Liquidus Surface of Quaternary Copper Phosphorus Brazing Filler Metals with Silver and Tin†

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

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

Abstract

Liquidus surface of copper phosphorus brazing filler metals with silver and tin addition was investigated. Micro vickers hardness of Cu-Ag-Sn-P quaternary filler metals was also measured. The kind of primary phase could be expected by using the phosphorus equivalent. The filler metals with the phosphorus equivalent more than 8.38 crystallized Cu_3P primary phase, whereas the filler metals with the value less than 8.38 crystallized copper solid solution. The primary phase was also predicted by the electron concentration of filler metal, and also the ratio of electron concentration of tin plus phosphorus content to that of copper plus silver content. The hardness of filler metal of as cast condition depended remarkably on the tin content.

KEY WORDS: (Brazing Filler Metals) (Copper Phosphorus Alloys) (Phase Diagrams) (Silver) (Tin) (Liquidus) (Hardness)

1. Introduction

The number of products brazed with copper phosphorus brazing filler metals are increasing instead of silver brazed products in order to save the production costs. Copper phosphorus filler metals can braze copper in an air atmosphere without the use of fluxes. The new filler metals with low melting points have been developed in these days[1)–4)], and brazing for iron has been also investigated[5)]. In previous work[6),7)], the phase diagrams of Cu-Ag-P and Cu-Sn-P systems were established by differential thermal analysis (DTA) and microscopic observations, consequently some cross sectional phase diagrams and liquidus surface at copper rich corner were obtained. However, in quaternary copper phosphorus filler metals with silver and tin the primary phase and liquidus temperature are not investigated preciely. The mechanical properties, erosion characteristics and spreadability are dependent on the microstructure and the kinds of primary phase of filler metals, therefore, the establishment of phase diagrams especially the liquidus surface is important for the selection of appropriate composition of filler metals with low melting temperature. From the point of view of the mechanical properties and erosion characteristics, the composition with copper solid solution primary phase is preferable to brazing filler metals.

The aim of the present study is to determine the primary phase and the liquidus temperature of quaternary filler metals with various composition, and to establish the liquidus surface plane of Cu-Ag-Sn-P quaternary alloys at copper rich region.

2. Experimental Procedures

Various Cu-Ag-Sn-P quaternary alloys were melted from pure copper, silver and tin with purity of 99.99 mass% or higher and Cu-15%P alloy (JIS H 2501), and then cast into the shape of rod of 5mm in diameter using mild steel mold. The alloys were melted in graphite crucibles under argon gas flowing atmospher. Chemical analysis of some cast alloys revealed that the compositions were almost the same as the nominal compositions.

The liquidus temperature was determined by DTA during cooling stage of the alloys. Vacuum encapsulated pure copper powder was used as a standard material. After solidification, the crystallized primary phase was determined by optical and scanning electron microscopic observations. The maximum amounts of each additional element are 25% for silver and tin 7% for phosphorus. In this paper the composition of the alloys are expressed by mass% if not especially mentioned.

† Received on April 26, 1989
* Instructor
** Professor
*** Faculty of Engineering, (Present address: Mitsubishi Motor Company Ltd.)

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

3. Results

3.1 Liquidus surface and microstructure of Cu-Ag-Sn-P quaternary alloys

Figure 1 shows the liquidus temperature and primary phase of the quaternary alloys with 5%P. The projection of the line that divides the primary phase of copper solid solution, (Cu), and intermetallic compound, Cu_3P, is illustlated by the broken line with a dot which started from 15%Sn-0%Ag(−5%P). The filler metals of the compositions on this broken line with a dot has the lowest liquidus temperature at a constant tin or silver content. Namely, the liquidus temperature lowered with increasing silver and tin content from the copper rich corner. On the other hand, in the region of primary Cu_3P phase, the liquidus temperature increased with increasing silver and tin content.

In Cu-25Ag-5Sn-5P filler metal primary silver solid solution phase, (Ag), was crystallized, therefore, the silver content that crystallizes the (Ag) primary phase at Cu-5%P alloy was measured from the Cu-Ag-Cu_3P tenary phase diagram[8]. The measured silver content was about 28.5%Ag, the point was plotted on the axis of Sn = 0% in Fig. 1. From the point the line which divides the primary phase into (Cu) and (Ag) was drawn by a straight broken line with a dot. The inclination of the line is the same as the line that divides the primary phase into (Cu) and (Ag) in Cu-Ag-P ternary phase diagram.

Figure 2 shows the examples of microstructure of quaternary alloys. From the difference of constrast of secondary electron image (SEI) and the characteristic X-ray image, it is evident that the alloys have four different phases. From the X-ray diffraction analysis, these phases were found to be Cu_3P, (Cu), $Cu_{41}Sn_{11}$ and (Ag). The

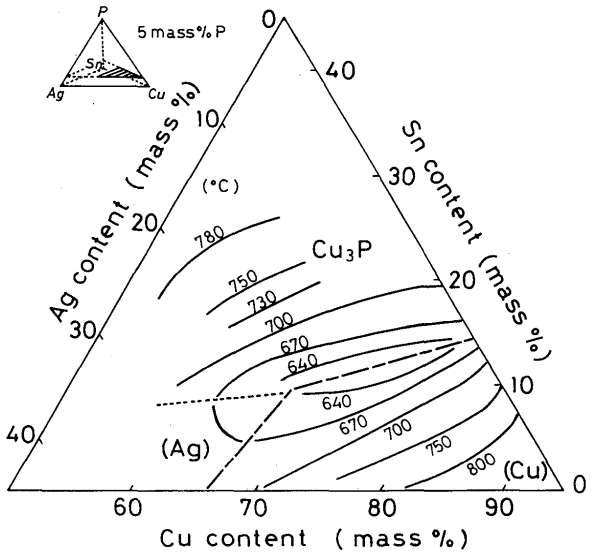

Fig. 1 Liquidus surface of Cu-Ag-Sn-P quaternary alloys with 5mass%P.

mean atomic number that can be calculated from the composition of each phase increased with this order, therefore, the color of the phase changed from dark to bright.

In 10Ag-10Sn alloy the large primary (Cu) phases were found. Eutectic Cu_3P phases were found surrounding the (Cu) phase. The amount of $Cu_{41}Sn_{11}$ phase was a little.

In 20Ag-10Sn alloy primary phase was Cu_3P. Relatively large (Cu) and (Ag) phases were found in ternary eutectic structure together with Cu_3P. In 10Ag-20Sn alloy the primary phase was Cu_3P, the amount of $Cu_{41}Sn_{11}$ increased, on the other hand the amount of (Cu) was extremely low.

From the microscopic observation the decrease of tin content increased the amount of (Cu) phase and decreased the amount of both $Cu_{41}Sn_{11}$ and Cu_3P phases at a constant phosphorus content. Silver also has the similar effect to tin but the degree is small.

3.2 Estimation of (Cu)/Cu_3P liquidus surface

The projection of cross line of (Cu) and Cu_3P primary phases to horizontal plane can be illustrated by a straight line in both Cu-Ag-P and Cu-Sn-P ternary alloys[7]. The solidification reaction on the line is $L \rightarrow L + (Cu) + Cu_3P$, of course the liquidus temperature is low on the line. Similarly in quaternary alloy with 5%P the projection of cross line of both primary phase plane to a horizontal plane can be illustrated by a straight line (Fig. 1).

In the previous report related to Cu-Ag-P and Cu-Sn-P ternary phase diagrams[7], addition of tin was found to have the similar effect to phosphorus addition relating to the kinds of primary phase, in the report the concept of phosphorus equivalent was introduced. The value of phosphorus equivalent was evaluated as 0.238 for tin and 0.066 for silver respectively in case the filler metal concentration was expressed by mass%. Under the hypothesis of the additive rule, phosphorus equivalent, P_{eq}, of quaternary alloy can be calculated from the following equation.

$$P_{eq}\ (\text{mass\%}) = [P] + 0.238\ [Sn] + 0.066\ [Ag]$$

where, [P], [Sn] and [Ag] are the content of each element, mass%.

If the values of phosphorus equivalent calculated from the above equation exceeded 8.38, which is the eutectic composition of phosphorus in Cu-P binary system, crystallization of primary Cu_3P phase is expected. On the contrary, in the alloys with the calculated value less than 8.38, crystallization of primary (Cu) phase is expected.

Figure 3 shows the primary phase planes of quaternary alloys with 3~7%P estimated by calculated values of phosphorus equivalent. The projections of dividing line of primary phase are shown by the dotted straight lines for

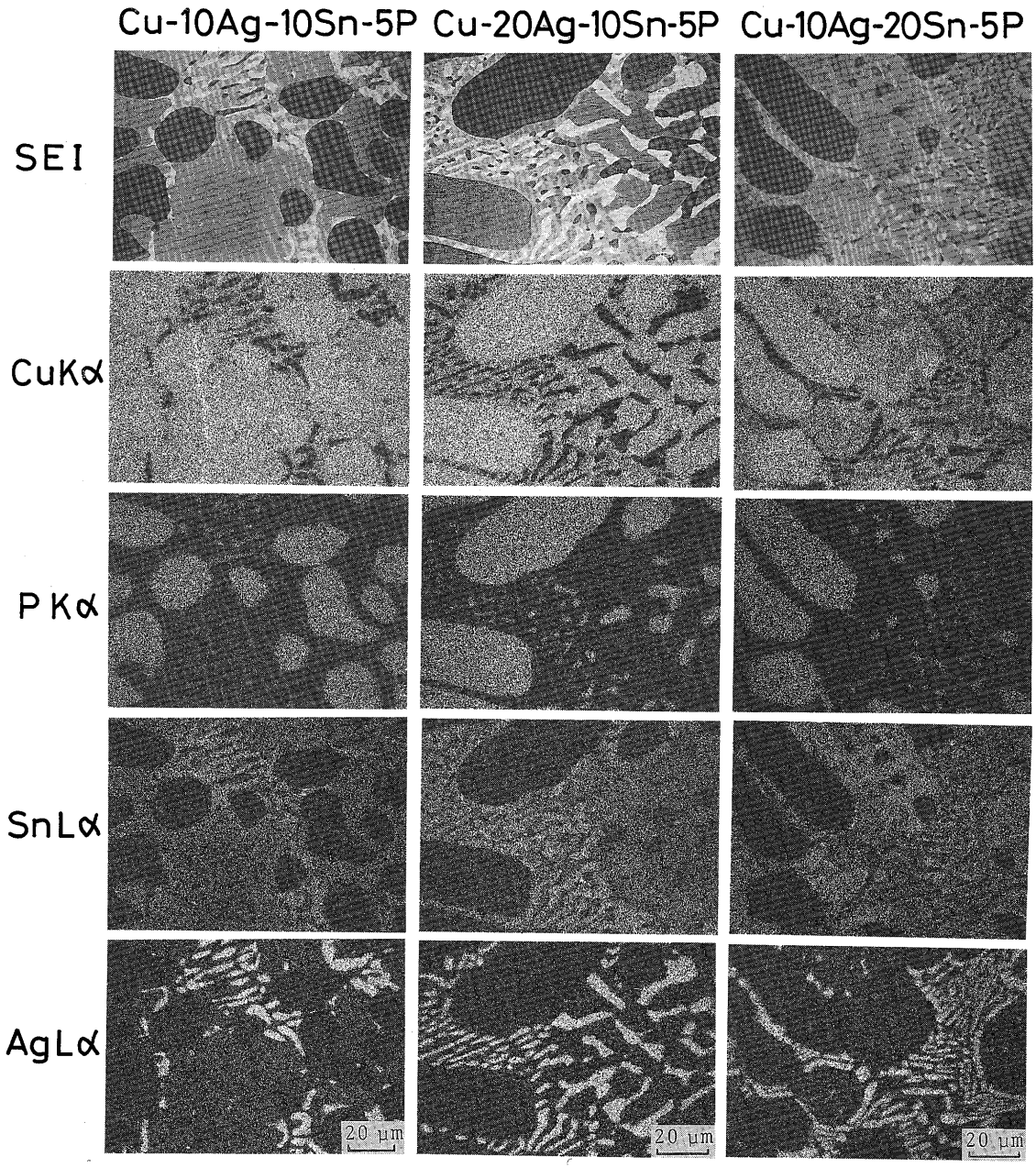

Fig. 2 Scanning electron micrographs and characteristic X-ray images of Cu-Ag-Sn-5P alloys after DTA.

each phosphorus content. The line dividing the (Cu) and (Ag) primary phase was constructed by refering the Cu-Ag-P and Cu-Sn-P ternary phase diagram as mentioned above. The dividing line of 5%P is well coincided with the experimental results shown in Fig. 1.

Figure 4 shows the primary phases, liquidus temperature and dividing line derived from calculation for 3.5%P alloy. The results are also well coincided with the experimental results. Accordingly the primary phase can be predicted from Fig. 3, which is derived from the phosphorus equivalent for arbitrary phosphorus content filler metals. At constant phosphorus content the alloys on the dotted lines has the lowest liquidus temperature.

3.3 Hardness

Figure 5 shows the micro vickers hardness of Cu-Ag-Sn-5P alloys of as cast condition. The hardness drastically increased with tin content, whereas the increment of silver content slightly decreased the hardness. In the alloys with 10%Sn, the hardness was almost similar irrespective of the primary phase, H_v = 254 ~ 281. The increase of silver content was effective to lower the hardness.

The hardness of 3.5%P alloys are listed in **Table 1**. The hardness is only slightly different with 5%P alloys, however, on the whole, the decrease in phosphorus content slightly decreased the hardness.

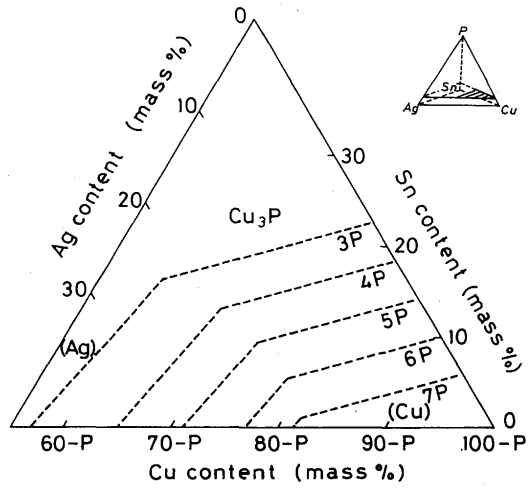

Fig. 3 Primary phase planes of Cu-Ag-Sn-P alloys with 3 ~ 7%P estimated by using phosphorus equivalent.

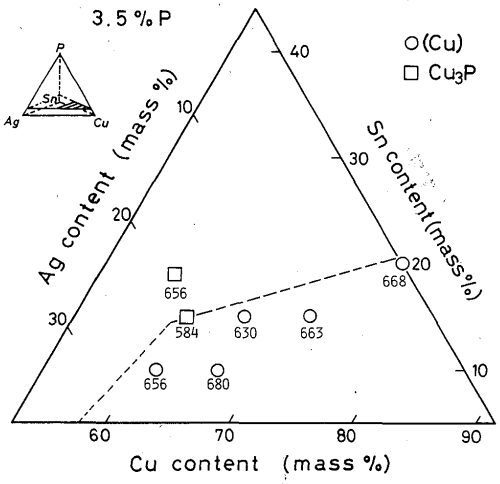

Fig. 4 Liquidus surface of Cu-Ag-Sn-P alloys with 3.5mass%P, numbers in the figure show the liquidus temperatures (°C).

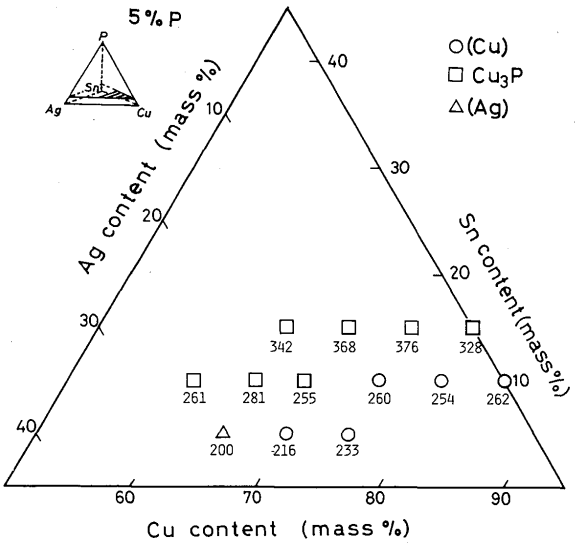

Fig. 5 Microvickers hardness of Cu-Ag-Sn-5P alloys of as cast condition.

Table 1 Microvickers hardness (H_V) of some Cu-Ag-Sn-P quaternary alloys with 3.5mass%P.

Alloys	H_V
Cu-25Ag-10Sn-3.5P	240
Cu-20Ag-10Sn-3.5P	238
Cu-20Ag-15Sn-3.5P	382
Cu-15Ag-15Sn-3.5P	356

Tin content has the greatest influence on the hardness. From the point of view of the workability, ductility and mechanical properties, the alloys with the hardness less than 300 would be preferable for brazing filler metals. Accordingly the tin content less than 15% should be chosen for practical use.

4. Discussions

The composition that the primary phase planes of (Cu) and Cu_3P cross will be discussed. The alloys with more phosphorus equivalent than a certain value is expected to crystallize primary Cu_3P phase. This concept is similar to the Hume-Rothery's rule[10]. The threshold value of the phosphorus equivalent is 8.38, eutectic phosphorus concentration of Cu-P binary system. The addition of silver, tin and/or phosphorus more than this threshold value might form Cu_3P primary phase. In the quaternary alloy the liquid phase exceeded the eutectic composition would crystallize primary Cu_3P phase.

The electron concentration, (*e/a*, *e*: valence number, *a*: number of atoms) of the intermetallic compound Cu_3P is calculated to be 8/4 = 2. On the contrary, the electron concentration of the filler metal, for example, 65Cu-15Ag-15Sn-5P alloy, is 1.71, that is lower than the value of Cu_3P. Under the hypothesis that Cu_3P with high electron concentration crystallizes in order to lower the electron concentration of coexisting liquid when the electron concentration of the liquid exceeds the certain value, the maximum or critical electron concentration of the liquid that can be torelable at liquidus temperature would be the value of Cu-P binary eutectic composition. The binary eutectic composition is Cu-8.38mass%P (Cu-15.8at%P), therefore, critical electron concentration, *e/a*, can be calculated as follows; *e/a* = (84.2 + 15.8 × 5)/100 = 1.632.

Both Cu-P and Cu-Sn systems form intermetallic compounds, however, Cu-Ag system only forms eutectic and shows no compounds. Accordingly, solution of silver into copper seems not to lower the solubility of the liquid. Thus when the ratio of the electron concentration of (Sn + P) to (Cu + Ag) in filler metal composition, ([Sn + P]/[Cu + Ag], exceeds a certain value, primary Cu_3P should

crystallizes. The critical value of [Sn + P]/[Cu + Ag] would be the same with the value of Cu-P binary eutectic, 15.8 × 5/84.2 = 0.9382.

Figures 6 and **7** show the results of estimation conducted by the two estimation parameters, *e/a* and [Sn + P]/[Cu + Ag] (for Cu-Sn-P ternary system [Sn + P]/[Cu + Ag] is [Sn + P]/[Cu]). The semicircles show that the estimated primary phase was (Cu), and the rectangles show the crystallization of primary Cu_3P phase was expected. Estimation by *e/a* is presented at top side and estimation by [Sn + P]/[Cu + Ag] is presented at bottom side. Open semicircles and open rectangles mean the coincidence of the estimation and the microscopic observation. Almost the majority of the filler metal showed good accordance with the estimation and microscopic observation, however, near the cross line of (Cu) primary phase plane and primary Cu_3P phase plane both results were not completely coincided, shown by the hatched lines. Dotted one is just on the cross line, therefore, both (Cu) and Cu_3P crystallized simultaneously.

The estimation about Cu-Ag-Sn-3.5P quaternary alloy also coincided well with the microscopic observation (**Fig. 8**).

The above results indicate that the composition with the value of 1.632 for *e/a* or 0.932 for [Sn + P]/[Cu + Ag] is closely near the (Cu)/Cu_3P cross line and the almost whole parts of filler metal showed eutectic like structure. Thus if the contents of two elements among silver, tin and

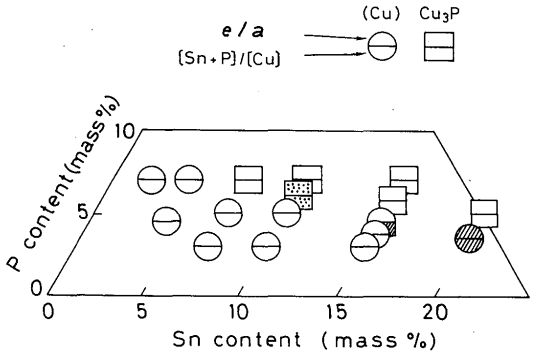

Fig. 6 Estimated primary phases by calculation of *e/a* and [Sn + P]/[Cu] for Cu-Sn-P system, open symboles show good agreement with microscopic observation, hatched ones appear to be inconsistent with observation, dotted one shows only eutectic like structure.

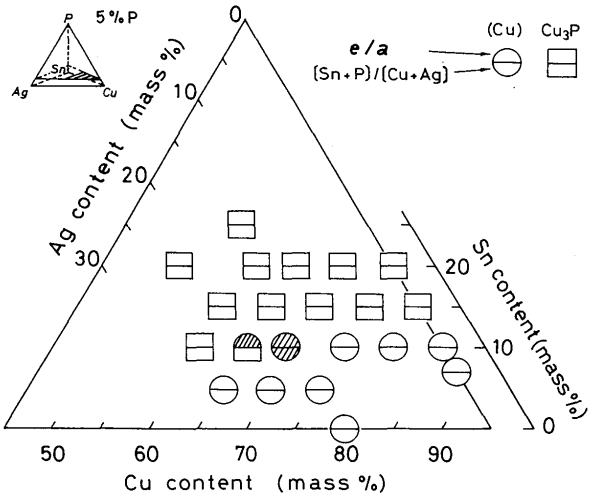

Fig. 7 Estimated primary phases by calculation of *e/a* and [Sn + P]/[Cu + Ag] for Cu-Ag-Sn-P system with 5mass%P, open symboles show good agreement with microscopic observation, hatched ones appear to be inconsistent with observation.

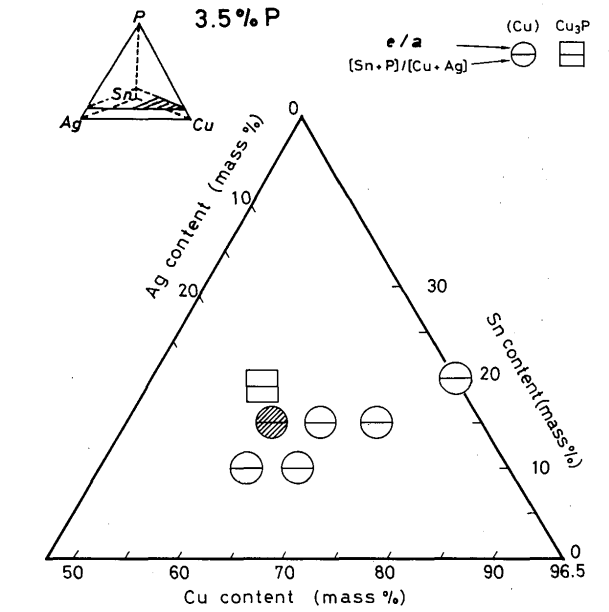

Fig. 8 Estimated primary phases by calculation of *e/a* and [Sn + P]/[Cu + Ag] for Cu-Ag-Sn-P system with 3.5mass%P, open symboles show good agreement with microscopic observation, hatched one appear to be inconsistent with observation.

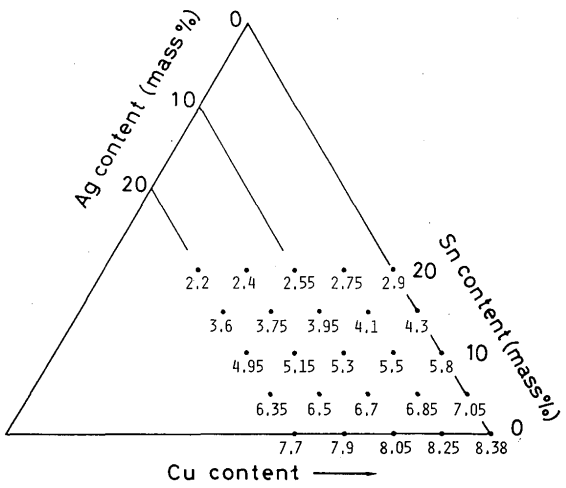

Fig. 9 Estimated minimum phosphorus content which crystalizes Cu_3P primary phase at various silver and tin content in Cu-Ag-Sn-P system, estimation made by calculation of [Sn + P]/[Cu + Ag]

phosphorus were fixed, balanced copper, the composition showing the lowest liquidus temperature could be withdrawn by the above mentioned estimation methods.

Figure 9 shows the minimum phosphorus content that crystallizes primary Cu_3P phase calculated by [Sn + P]/[Cu + Ag]. As mentioned above, the liquidus temperature became the lowest at the shown phosphorus value at given silver and tin content. The liquidus temperature increased with increasing tin and silver content. The results of the present work gives the appropriate phosphorus concentration at any given silver and tin content in Cu-Ag-Sn-P quaternary system.

The reason of the good agreement of the estimation results obtained by the methods, calculation by e/a and [Sn + P]/[Cu + Ag], is not clear, however, these estimation methods offers the important information of the kind of primary phase ((Cu) or Cu_3P) and the composition with relatively low melting point in Cu-Ag-Sn-P quaternary system relatively complexed.

5. Conclusions

The liquidus surface of Cu-Ag-Sn-P quaternary alloys for brazing filler metal was established to clarify the primary phase planes and to know the low melting temperature ranges. The results are summarized as follows.

(1) The estimation of primary phase of Cu-Ag-Sn-P alloys could be achieved by using the phosphorus equivalent of silver and tin. Phosphorus equivalent, P_{eq}, is calculated by the following equation.

$$P_{eq}(\text{mass\%}) = [\text{mass\%P}] + 0.238\ [\text{mass\%Sn}] + 0.066\ [\text{mass\%Ag}]$$

At the phosphorus equivalent of 8.38, binary eutectic appears; and in the range of $P_{eq} > 8.38$, primary Cu_3P crystallizes; and in the range of $P_{eq} < 8.38$, primary (Cu) crystallizes. The available composition range of this estimation is less than 25%Sn, less than 20%Ag and more than 3%P.

(2) The electron concentration, e/a, and the electron concentration ratio of (Sn + P) to (Cu + Ag) in filler metal composition, [Sn + P]/[Cu + Ag], were also found to be useful for the estimation of primary phase. If these values exceeded the values of Cu-P binary system, primary Cu_3P phase would crystallizes. The estimations by these electron concentration coincided well with the estimation by phosphorus content and microscopic observation.

(3) The above mentioned results concludes that the estimation methods of primary phase of Cu-Ag-Sn-P quaternary system are established; available range is less than 25%Sn, less than 20%Ag and more than 3%P. The phosphorus content that offers the minimum liquidus temperature at a given arbitrary silver and tin contentration can be derived by these estimating calculation methods.

(4) The hardness of Cu-Ag-Sn-P alloys of as cast condition depended on mainly tin concentration. The micro vickers hardness of the alloys with 15%Sn exceeded 300, therefore, the filler metals with less than 15%Sn would be suitable for practical use.

Acknowledgment

The authors would express our hearty thanks to Mr. S. Kawaguchi at Tanaka Precious Metals Products and to Mr. Y. Watanabe and Mr. K. Oishi at Sambo Copper & Brass Co., Ltd. for preparing samples.

References

1) I. Okamoto, T. Takemoto, T. Yasuda and T. Haramaki: "Copper Phosphorus Brazing Filler Alloys with Low Melting Temperature, Report-I", J. Weld. Soc. Japan, Vol. 49 (1980), No. 9, 642–647 (in Japanese).
2) Tanaka Precious Metals Products: "Filler Metals & Fluxes", (1981), 11.
3) Neis Corporation: "Materials for Low Temperature Gas Welding", (1980), 15.
4) A. Datta, A. Rabinkin and D. Bose: "Rapidly Solidified Copper-Phosphorus Base Brazing Foils", Weld. J., Vol. 63 (1984), No. 10, 14–21.
5) R.D. Mottram, A.S. Wronski and A.C. Chilton: "Brazing Copper to Mild Steels Using Copper-Phosphorus-Tin Pastes, Weld. J., Vol. 65 (1986), No. 4, 43–46.
6) T. Takemoto, I. Okamoto and J. Matsumura: "Copper Phosphorus Brazing Filler Metals with Low melting Temperature, Report-II", Q.J. Japan Weld. Soc., Vol. 5 (1987), No. 1, 81–86 (in Japanese).
7) T. Takemoto, I. Okamoto and J. Matsumura: "Phase Diagrams of Cu-Ag-P and Cu-Sn-P Ternary Brazing Filler Metals", Trans. JWRI, Vol. 16 (1987), No. 2, 301–307.
8) K.M. Weigert: "Physical Properties of Commercial Silver-Copper-Phosphorus Brazing Alloys", Weld. J., Vol. 35 (1956), No. 7, 672–674.
9) E. Gebhardt und G. Petzow: "Über den aufbau des Systems Silver-Kupfer-Zinn", Z. Metallkde., Vol. 50 (1959), No. 10, 597–605.
10) for example, H. Sudoh, I. Tamura and T. Nishizawa: "Microstructure of Metals", Maruzen, (1981), 90 (in Japanese).