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Studies on Dissolution of Metal Element from Flux (Report-I) †
—— Dissolution of Ag to Molten Tin and Tin Base Binary Alloys ——

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Abstract

The effect of temperature on transfer of Ag from Ag_3PO_4-$SnCl_2$ system flux to molten tin (or Sn base binary alloys) was studied. It was influenced on the dissolution of Cu from Cu base metal, which increased with raising temperature. Moreover, in order to know the change in composition of solder after soldering of Cu plates when Ag_3PO_4-$SnCl_2$ system was used as flux, the transfer of Ag element from the flux and loss of alloying metal containing in solder binary alloys were considered on the basis of the chemical reaction between flux and alloys.

The reaction of flux with alloys might be explained by the electro-chemical series of alloying metals in the molten flux containing the alloy. It was made known that the composition of solidified solder was greatly changed by the reaction.

1. Introduction

During the course[1, 2] of investigation on the flux action of soldering, it was elucidated that the reaction (eq.1) of metallic salt with molten Sn occurred during spreading test and metal produced by the reaction dissolved in Sn solder during spreading test.

$$\text{Metal salt} + \text{Sn} \xrightarrow{\Delta} \text{Sn salt} + \text{Metal}-(\text{Sn}) \quad (1)$$

Moreover, the reaction and dissolution were important factors controlling spread and wet. Then, the phenomena take place that after spreading the composition of solder changes greatly by the dissolution of metal from flux, when copper base metal is soldered with various combinations of metallic salt and solder.

In order to know whether the reaction and the dissolution of metal from flux effected to spreading of the solder or not, it is required to know the composition of the solder after spreading test.

So, in this report, the content of Ag from flux in solidified Sn or Sn base alloys on copper plate was confirmed mainly by EPMA when Ag_3PO_4-$SnCl_2$ salt was used as flux. In the case of Sn solder, the effects of flux concentration and heating temperature on the disolution of Ag were investigated. The dissolution was considered on the basis of the chemical reactions between Sn (or alloying metal) and Ag_3PO_4 (or $SnCl_2$).

2. Experimental apparatus and procedures

Commercially available reagent-grade metallic salts and Sn base binary alloys were used in this investigation.

Table 1 Melting points of fluxes and alloys used in this experiment

Flux	Mp (decomp.), °C	Alloy, wt%	Mp, °C
$SnCl_2$	247	50Sn - 50Zn	345
40KCl-60LiCl eutectic	356	81Sn - 19Cd	195
		55Sn - 45In	136
Ag_2SO_4	652	62Sn - 38Pb	183
Ag_2CO_3	(218)	50Sn - 50Bi	155
Ag_3PO_4	849		

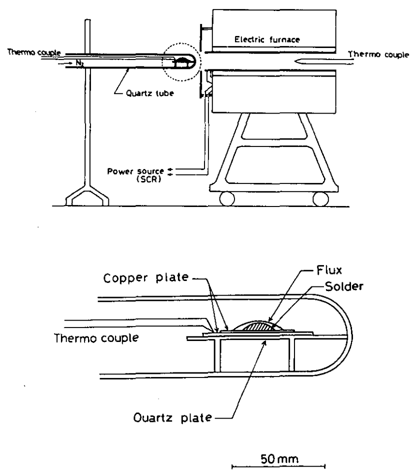

Fig. 1 Apparatus for spreading test

Their physical properties are shown in Table 1. The used copper plate (38x38x0.5mm, JIS CuP-1, 99.9%) was electro-polished, and grease and dust were removed by use of acetone just before the spreading test. As shown in Fig. 1, Sn(100mg) or Sn base binary alloy (100mg) and

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metallic salt (200mg) were placed in the center of Cu plate on the quartz boat at a controlled temperature. The specimens were heated to required temperature and maintained for 1 min., and then removed and cooled. The dissolution amount of Ag from metallic salt and the decrease amount of alloying metal containing in solidified Sn base alloy were elucidated by EPMA.

3. Results and Discussions

3.1 Effects of flux concentration and heating temperature on dissolution of Ag from Ag_3PO_4-$SnCl_2$ salt into Sn solder

By the studies[3)] on flux action in soldering, it was certified that silver salt reacted with molten Sn as shown in eq- (2) to make Ag metal dissolved in molten Sn.

$$\text{Ag salt} + \text{Sn} \xrightarrow{\Delta} \text{Sn salt} + \text{Ag-(Sn)} \qquad (2)$$

However, the effect of metallic salt composition ($Ag_3PO_4/SnCl_2$) or heating temperature on dissolution process of Ag is not yet known.

In this section, Ag dissolution in Sn was investigated in order to elucidate the variation of solder composition after spreading, using the above mentioned flux. As metallic salts, 10mol% Ag_3PO_4/90mol% $SnCl_2$, 20mol% Ag_3PO_4/80mol% $SnCl_2$ and 30mol% Ag_3PO_4/70mol% $SnCl_2$ were used, when spreading tests were done at 400° 500°C and 600°C respectively. After these tests, the amount of Ag dissolved to the spread solder was measured by analyzing the cross section of specimens by EPMA. The results are as shown in Table 2. Cu in the table is from Cu base metal. Moreover, in Figs. 2, 3 and 4, line analysis results of Ag and Cu in deposited alloy are the case of tests made at 400°C, 500°C and 600°C with 20mol% Ag_3PO_4/80mol% $SnCl_2$ respectively. The effect of heating temperature on dissolution of Ag and Cu are shown in Figs. 5 and 6, reploted from results in Table 2. The data of 400°C with 30mol% Ag_3PO_4 shown in Table 2 was omitted, since the salt did not melt completely, and did not wet Sn on Cu plate. From Figs. 5 and 6, the dissolution amount of Cu in solidified Sn increases with raising temperature, especially at 600°C, a great deal of Cu dissolves in Sn solder, so that Ag dissolution from flux was decreased by the dissolution of a great amount of Cu from base metal.

Depending on the dissolubility of Cu to Sn and the reactivity between Sn and Ag_3PO_4, maximum dissolution of Ag in deposited Sn is observed at 500°C. Namely, the dissolution of Ag increases with upward tendency of temperature, due to the increase of reactivity between Ag_3PO_4 and Sn. However, especially at 600°C, that of Ag is suppressed greatly by the dissolution of Cu from base metal. The reaction of Sn with Ag_3PO_4 occurred as shown in eq-(3).

$$2Ag_3PO_4 + 3Sn \xrightarrow{\Delta} Sn_3(PO_4)_2 + 6Ag \qquad (3)$$

Similar tests were done, using various $Ag_2SO_4/SnCl_2$ and $Ag_2CO_3/SnCl_2$ system fluxes. Then, Cu-Ag-Sn ternary alloys obtained by the dissolution of Ag from such various silver salts as Ag_3PO_4, Ag_2CO_3 are shown in Fig. 7. The composition of these deposited alloys was measured by EPMA. When Ag_2SO_4 or Ag_2CO_3 was used, the dissolution of Ag in deposited Sn is dependent on both the dissolubility of Cu to Sn and the reactivity between Sn and silver salts as well as in the case of Ag_3PO_4.

Table 2 Composition of solder after spreading, using various concentrations of Ag_3PO_4 fluxes

Concentration of flux	Test temp. (° C)	Approximate composition by EPMA (wt%)		
		Ag	Sn	Cu
10 MOL%	400	27	58	15
	500	33	41	26
	600	4	32	64
20 MOL%	400	20	71	9
	500	30	56	14
	600	10	28	62
30 MOL%	400	–	–	–
	500	41	43	16
	600	25	20	55

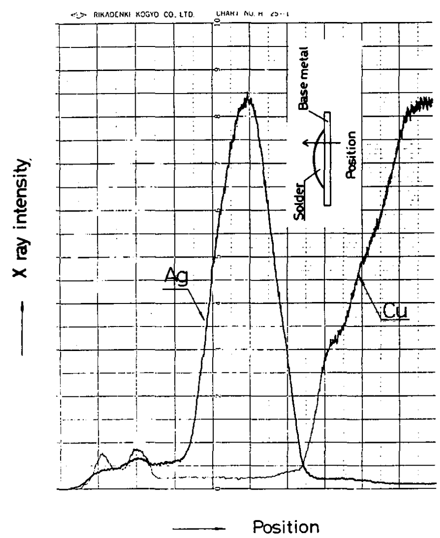

Fig. 2 Distribution of Ag dissolved from 20mol% Ag_3PO_4 flux in Sn solder on Cu plate at 400°C

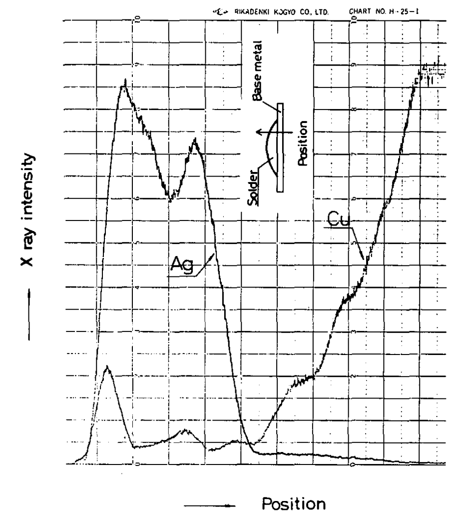

Fig. 3 Distribution of Ag dissolved from 20mol% Ag_3PO_4 flux in Sn solder on Cu plate at 500°C

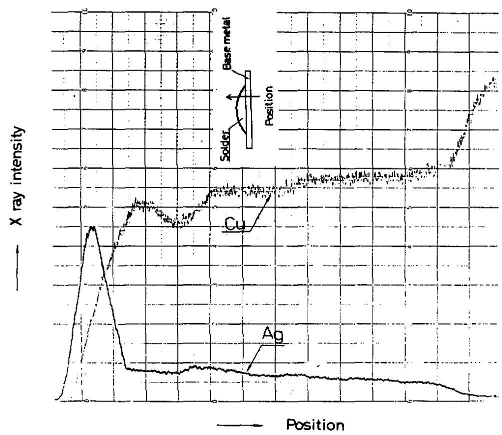

Fig. 4 Distribution of Ag dissolved from 20mol% Ag_3PO_4 flux in Sn solder on Cu plate at 600°C

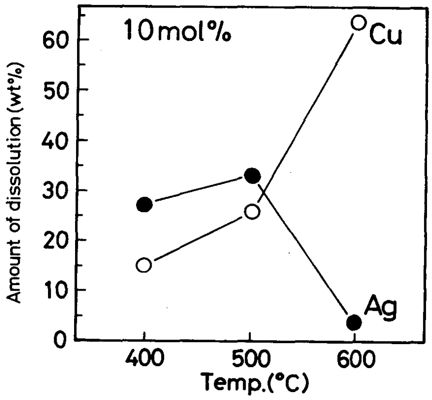

Fig. 5 Effect of heating temperature on dissolution of Ag and Cu when 10mol% Ag_3PO_4 was used as flux

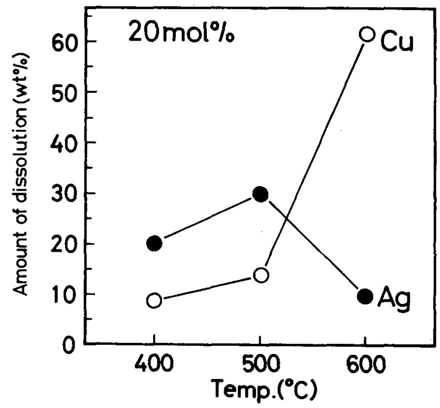

Fig. 6 Effect of heating temperature on dissolution of Ag and Cu when 20mol% Ag_3PO_4 was used as flux

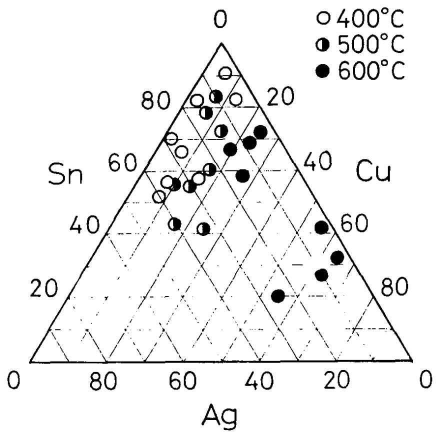

Fig. 7 Composition of spread solder on Cu plate, using various concentrations of Ag salt mixing fluxes and temperatures

3.2 Dissolution of Ag in Sn base binary alloys from $Ag_3PO_4/SnCl_2$ system salt

It was elucidated that the dissolution of Ag from various silver salts to Sn is dependent greatly on heating temperature or flux concentration. In this section, the effect of metal addition to Sn on dissolution of Ag in Sn-base binary alloy, using Ag_3PO_4-$SnCl_2$ salt as flux, was investigated on the basis of the reactivity between Sn (or alloying metal) and Ag_3PO_4 (or $SnCl_2$). Moreover, the compositions of various Sn-Metal-Ag-Cu alloys obtained by the reaction between Sn base binary alloy and silver salt, were elucidated by EPMA.

3.2.1 Dissolution of Ag in Sn base binary alloys

In order to know the effect of alloying metal in Sn base binary alloys on dissolution of Ag, spreading tests were tried at 500°C, for Sn base binary alloys containing various metals (Pb, Bi, Zn, Cd etc.) and 20mol%Ag_3PO_4-80mol%$SnCl_2$ flux.

The spreading test was done by the same method as mentioned in previous section. 20mol%Ag_3PO_4--80mol%$SnCl_2$ (200 mg) and Sn base binary alloy (100 mg) were placed on copper plate as shown in Fig. 1. The specimen was heated to 500°C and maintained for 1 min. After cooling, the dissolution of Ag and the loss of alloying metal in spread solder were checked by analyzing the cross section of specimen by EPMA. The results are shown in Table 3. Line analysis results of Ag and various metals in solder before and after spreading test are shown in Fig. 8 and Fig. 9, respectively, for Sn-In and Sn-Bi alloys. From Table 3, we note that alloying metal in Sn base binary alloy decreases substantially for each alloy after spreading tests. Moreover, Ag dissolves in every Sn base binary alloy from Ag_3PO_4. However, the amount of Ag in Sn base alloy after spreading is varied greatly with the kind of alloying element in Sn base binary alloy. Namely, the dissolution of Ag in deposited Sn base alloy was promoted strongly, when Bi or Pb was added to Sn as alloying element.

On the other hand, in Sn-Zn and Sn-Cd alloys, the dissolution amount of Ag is less than in any other solders. In order to know precisely the relation between the dissolution amount of Ag and the weight loss of alloying metal or Sn, the composition values of four elements shown in Table 3 were converted as ternary Ag-Sn-Metal alloy, excluding Cu from base metal.

The amount of Ag and weight loss of alloying metal in these ternary alloys were shown in Fig. 10. From the figure, it is observed that the amount of Ag in Sn-Cd alloy and Sn-Zn alloy does not increase in proportion to Cd or Zn decreases. However, the amount of Ag in Sn-Bi alloy and Sn-Pb alloy increases with the increase of weight loss of Bi or Pb. The amount of Ag dissolved from Ag_3PO_4 depends greatly on the kind of metals added to Sn. Since the conditions of spreading tests are quiet constant, the difference may be considered to be due to the reactivity between $SnCl_2$-Ag_3PO_4 salt and molten Sn base alloy containing Cu dissolved from base plate.

Namely, the dissolution of Ag depends upon whether alloying metal in molten Sn base binary alloy reacts with either Ag_3PO_4 or $SnCl_2$. In the case of Sn-Cd alloy and Sn-Zn alloy, Zn and Cd react mainly with $SnCl_2$ as shown in eqs (3) and (4), since Zn and Cd appear to be more base than Sn in this molten salt. As the result of the reaction, dissolution amount of Ag in Sn-Zn and Sn-Cd alloys is found small.

$$Zn + SnCl_2 \xrightarrow{\Delta} ZnCl_2 + Sn \quad (3)$$

$$Cd + SnCl_2 \xrightarrow{\Delta} CdCl_2 + Sn \quad (4)$$

However, in the case of Sn-Pb alloy and Sn-Bi alloy, Pb and Bi in these alloys barely react with $SnCl_2$, but reacted chiefly with Ag_3PO_4 as shown in eqs. (5) and (6), because Pb and Bi become more noble than Sn, and more base than Ag in molten salt.

$$3Pb + 2Ag_3PO_4 \xrightarrow{\Delta} Pb_3(PO_4)_2 + 6Ag \quad (5)$$

$$Bi + Ag_3PO_4 \xrightarrow{\Delta} BiPO_4 + 3Ag \quad (6)$$

From the above results, it was elucidated that the dissolution of Ag in Sn base binary alloys from Ag_3PO_4-$SnCl_2$ was dependent on the reactivity between either Sn or metal in the binary alloy on one side and either Ag_3PO_4 or $SnCl_2$ in the salt on the other. The reaction may be explained by electro-chemical series of metal contained in Sn base binary alloy in molten salt.

Table 3 Compositions of solder after spreading, using 20mol% Ag_3PO_4-$SnCl_2$ system flux

Sn-Metal Alloys	Approximate composition by EPMA (wt%)			
	Ag	Sn	Cu	Metal
50Sn - 50 Zn	10	49	19	22
81Sn - 19Cd	1	80	15	4
Sn	38	49	13	–
55Sn - 45In	29	35	33	3
62Sn - 38Pb	45	31	21	3
50Sn - 50Bi	45	25	15	15

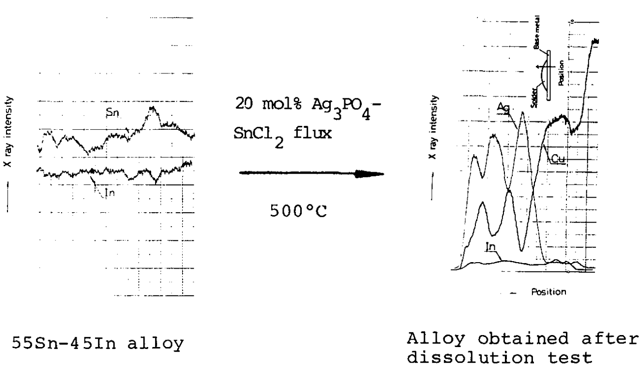

Fig. 8 Distribution of alloy elements of 55Sn-45In alloy itself and dissolution of Ag from 20mol% Ag_3PO_4-$SnCl_2$ system flux in the alloy spread on Cu plate

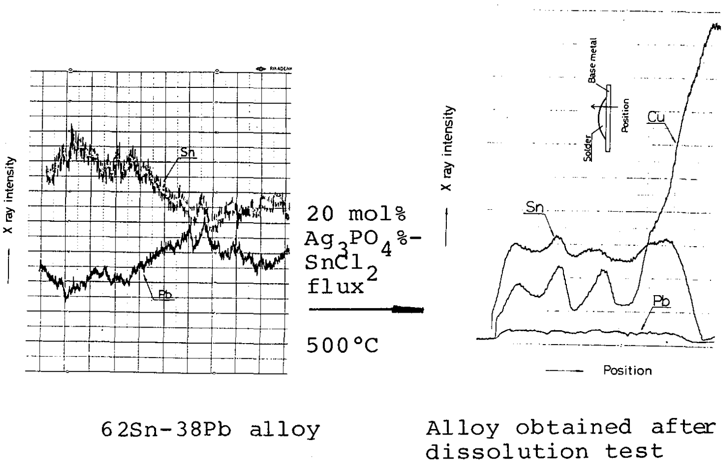

Fig. 9 Distribution of alloy elements of 62Sn-38Pb alloy itself and dissolution of Ag from 20mol% Ag_3PO_4-$SnCl_2$ system flux in the alloy spread on Cu plate

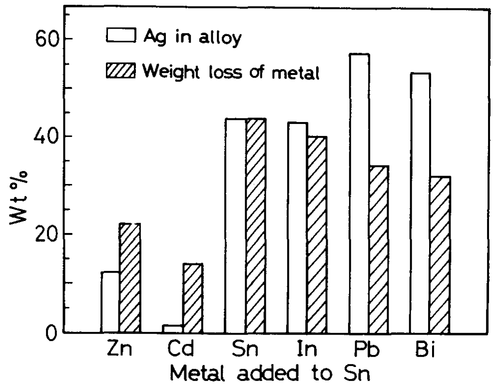

Fig. 10 Effect of alloying metal on dissolution of Ag and weight loss of alloying metal in Sn base binary alloy

4. Conclusion

When Ag_3PO_4-$SnCl_2$ system salt was used as flux, and Sn or Sn base binary alloy was used as solder, the dissolution of Ag from flux in deposited solder, which contained copper dissolved from base metal, and the loss of alloying element were found to be dependent on mainly the reactivity between either Ag_3PO_4 or $SnCl_2$ on one side and either Sn or metal on the other. It should be emphasized that the composition of solder deposited in copper base plates with a mixing flux of silver salt system and a tin base solder varies by the dissolution of silver constituent in the flux and of the base plate constituent.

References

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