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Studies on Dissolution of Metal Element from Flux (Report II) †
—Dissolution of Ag to Molten Zn-Cd Alloys—

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Abstract

The dissolution of silver from various fluxes into various Zn-Cd alloys was studied in order to obtain a joint of similar compositions as the compositions of BAg filler metal. When 77wt%Zn-23wt%Cd alloy is used as solder, similar compositions as the compositions of BAg-1 were obtained on copper base plate at 600°C with $Ag_3PO_4/LiCl\text{-}KCl$ system eutectic flux, and the content of silver dissolved in the alloy was affected by the dissolution of copper base plate.

1. Introduction

Various metals can be joined at comparatively lower temperature by soldering or brazing than by welding. Namely, the joining can be carried out without almost dissolving of the base metal and changing of the physical properties of joined part. Especially, silver brazing has been used widely due to good wettability for various base metals and higher mechanical strength of the brazed joint. In previous paper,[1] it was noticed that a great amount (about 40wt%) of silver dissolved into tin or Sn-Metal alloys, which were used as solders, from silver salt system flux, which was dissociated by eq. (1).

$$\text{Ag salt} + \text{Sn} \longrightarrow \text{Sn salt} + \text{Ag} \quad \ldots\ldots (1)$$

The compositions of BAg filler metals are chiefly silver, copper and zinc. So, in this report, the dissolution of silver from flux into various Zn-Cd alloys was investigated under the consideration of eq. (2) and also in order to obtain the solidfied metal of similar compositions as BAg filler metal when the Zn-Cd alloy is used as solder.

$$\text{Ag salt} + \text{Zn} \longrightarrow \text{Zn salt} + \text{Ag} \quad \ldots\ldots (2)$$

2. Experimental Apparatus and Procedures

The dissolution process of silver, copper and nickel into Zn-Cd alloys from flux was carried out by the same method as that in previous paper[2]. The dissolution amount of silver, copper and nickel in the spread metal was measured by EPM analyzing at the cross section of specimens obtained by spreading test. The used base plates were pure copper (JIS, CuP-1, 99.96%) and pure nickel (99.6%), and the size is 38 x 38 x 0.5 mm. The base plates were polished with No. 800 (JIS) emery paper before spreading test. Commercially available reagent grade $SnCl_2$, LiCl, KCl and various silver salts were used as flux. Table 1 shows the melting and decomposition points of various fluxes and solders used.

Table 1 The properties of fluxes and alloys used in this experiment

Flux	mp(decomp.), °C	Alloy, wt%	mp, °C
$SnCl_2$	247	84Sn–16Zn	245
$ZnCl_2$	318	50Sn–50Zn	345
$NiCl_2$	1030	14Zn–86Cd	275
40KCl–60LiCl	356	58Zn–42Cd	334
eutectic		77Zn–23Cd	360
Ag_2SO_4	652		
Ag_2CO_3	(218)		
Ag_3PO_4	849		

3. Results and Discussions

3.1 Effect of flux composition and heating temperature on dissolving of silver into molten Zn-Cd alloys

In order to make clear the composition change of metal solidfied in a joint of copper base plates when the

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combination of solder and flux is changed variously, the dissolution of metals from flux and base metal into solidfied solder was studied. In this experiment, Zn-Cd solders and silver salt fluxes were used. With various combinations, the solidfied metal of similar compositions as BAg filler metal (composed of Ag, Cu, Zn and Cd) may be obtained by dissolving silver produced from the reaction between solder and flux.

3-1-1 Dissolution of silver into molten pure zinc or pure cadmium

At the first time, the dissolving of silver into molten zinc reacted with various silver salt fluxes was examined. In the case of pure zinc, BAg-5 filler metal (composed of Ag, Cu and Zn) may be considered to be given by the reaction between zinc and silver salt. The result are shown in Table 2. From the table, a great amount of tin are

Table 2 Compositions of Cd or Zn solders spread on copper base plate with silver salt system fluxes at 500°C

Metal	Flux	Approximate composition by EPMA(wt%)				
		Ag	Sn	Cu	Zn	Cd
Cd	20mol% $Ag_3PO_4-SnCl_2$	2	10	6	–	82
	20wt% $Ag_2SO_4-(KCl^*/LiCl)$	25	–	4	–	71
Zn	20mol% $Ag_3PO_4-SnCl_2$	16	20	19	45	–
	20wt% $Ag_3PO_4-ZnCl_2$	7	–	28	65	–

* KCl-LiCl eutectic salt

observed in the zinc solder obtained after the reaction between Ag_3PO_4-$SnCl_2$ system flux and zinc solder. As shown in previous paper,[2)] the result is explained from the reaction that tin shown in eq. (3) again dissolved in molten zinc.

$$SnCl_2 + Zn \longrightarrow ZnCl_2 + Sn \qquad (3)$$

However, the surface of the zinc solders obtained with other fluxes except for $SnCl_2$ base flux becomes porous and the wetting phenomena of those solders on the copper plate are not almost observed. The reason is believed to be due to the formation of oxide film on the molten zinc solder and the oxide film is formed by poor reactivity of flux used.

Next, pure cadmium, which is more noble than zinc, was used as solder to control the reaction with silver salt. The result is shown also in Table 2. The line analysis of alloy elements of the cadmium solder after spreading test made on the copper base plate is shown in Fig. 1. From the distributions of cadmium and silver, the formation of compound (perhaps, ε phase), in which a few percentage of copper dissolves, of Ag-Cd alloy in the spread solder is considered, however, we note that the spread solders obtained with the combination of various silver salt fluxes and zinc or cadmium solder contain less silver than commercial BAg filler metal.

In next section, Zn-Cd binaly alloys were used as solder, namely, it is expected that silver content in the spread metal may be controlled by mutual action between zinc and cadmium.

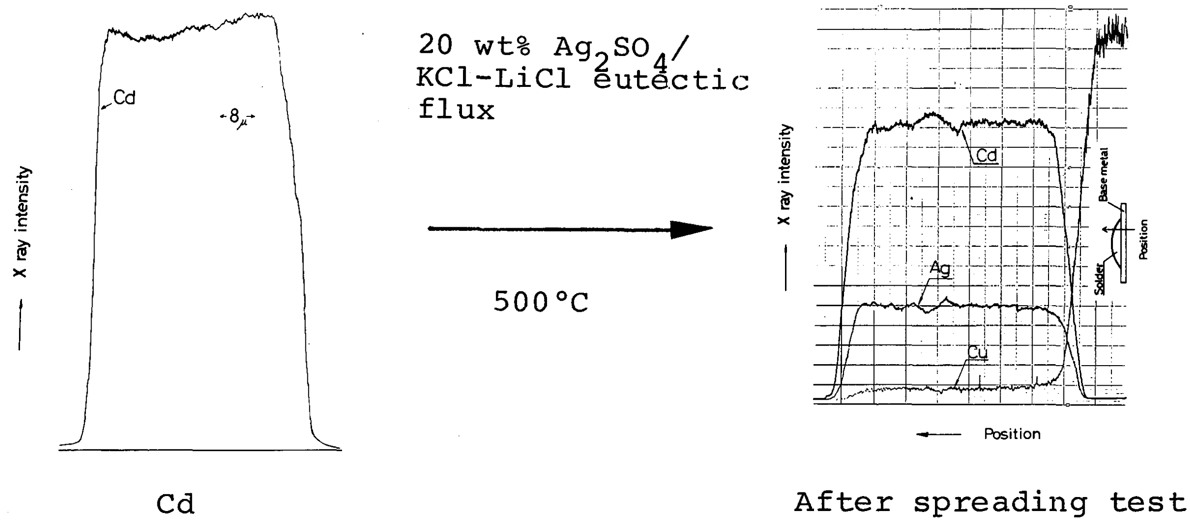


Fig. 1 Distributions of Ag, Cd and Cu in pure cadmium spread on copper base plate with 20wt% Ag_2SO_4/ KCl-LiCl eutectic system flux

3-1-2 Dissolution of silver into molten Zn-Cd binaly alloys

In the case of 14wt%Zn-86wt%Cd alloy, the effect of flux composition on the dissolving of silver into the alloy was studied. The results are shown in Table 3. When

Table 3 Compositions of 86Cd–14Zn solder spread on copper base plate with various fluxes at 500°C

Flux	Approximate composition by EPMA(wt%)				
	Ag	Sn	Cu	Zn	Cd
20wt% Ag_2SO_4–(KCl*, LiCl)	21	–	7	2	70
20wt% Ag_2CO_3–(KCl*, LiCl)	19	–	12	no detect	69
20wt% Ag_3PO_4–(KCl*, LiCl)	19	–	16	7	58
30wt% Ag_3PO_4–(KCl*, LiCl)	26	–	15	6	53
30mol% Ag_3PO_4–$SnCl_2$	7	19	40	3	31

* KCl-LiCl eutectic salt

30wt%Ag_3PO_4/KCl-LiCl eutectic system flux is used, a desirable result was obtained by the dissolution of silver. Therefore, for the other Zn-Cd binaly alloys shown in Table 1, the effect of heating temperature on the dissolution of silver was investigated for each base metal (Cu, Ni), using the above mentioned flux. The results are shown in Table 4 and Table 5, respectively for 58wt%Zn-42wt%Cd and 77wt%Zn-23wt%Cd alloys. As shown in both tables, two layers (A and B), which are well known already, are formed at interface between solder and base metal and A layer is chiefly composed of zinc and the component of each base metal. When these compositions of the spread metal are compaired with the compositions of commercial BAg filler metal, the content

Table 4 Compositions of 42Cd–58Zn solder spread on Cu or Ni plate with 30wt% Ag_3PO_4/KCl–LiCl eutectic system flux

Base metal	Test temp. (°C)	See Fig.3	Approximate composition by EPMA(wt%)				
			Ag	Cd	Zn	Cu	Ni
Cu	400	B	22	28	45	5	–
	500	B	18	33	36	13	–
	600	A	2	3	49	46	–
		B	25	38	21	16	–
Ni	400	A	1	no detect	89	–	10
		B	13	42	41	–	4
	500	A	2	1	85	–	12
		B	23	49	28	–	no detect
	600	A	1	1	76	–	22
		B	23	49	26	–	2

Table 5 Compositions of 23Cd–77Zn solder spread on Cu or Ni plate with 30wt% Ag_3PO_4/KCl–LiCl eutectic system flux

Base metal	Test temp. (°C)	See Fig.3	Approximate composition by EPMA(wt%)				
			Ag	Cd	Zn	Cu	Ni
Cu	400	B	12	12	65	11	–
	500	B	22	22	41	15	–
	600	A	4	3	47	46	–
		B	41	20	22	17	–
Ni	400	A	2	1	86	–	12
		B	19	27	53	–	1
	500	A	2	1	83	–	14
		B	20	38	42	–	no detect
	600	A	5	1	78	–	16
		B	32	22	45	–	1

(41wt%; See Table 5) of silver in 77wt%Zn-23wt%Cd alloy spread on the copper base plate at 600°C is similar to BAg filler metal. Line analysis results of Ag, Cu and Zn in the solder before and after spreading test are shown in Fig. 2. Figure 3 is schematic explanation of the cross

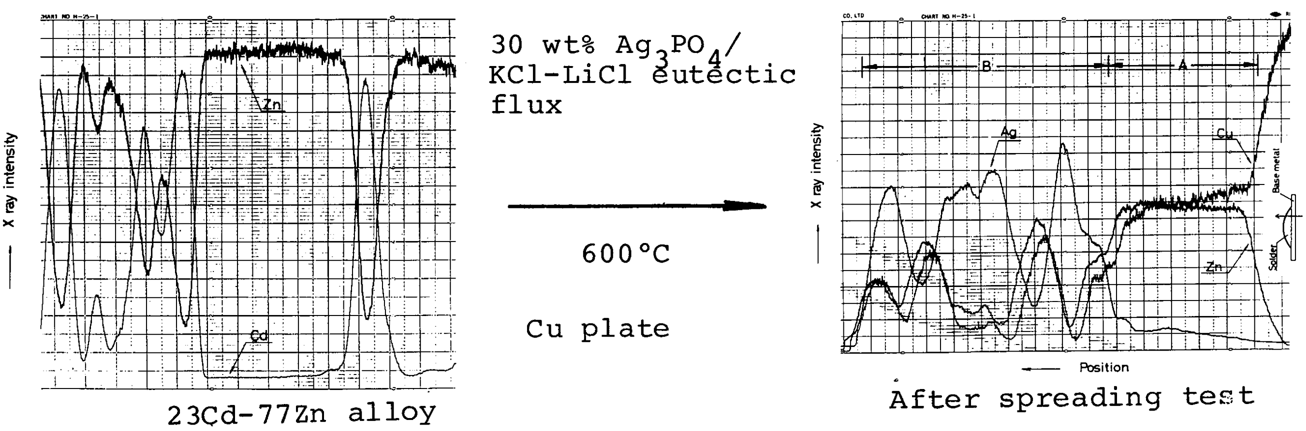


Fig. 2 Distributions of Ag, Cu and Zn in 77Zn-23Cd alloy spread on copper base plate with 30wt% Ag_3PO_4/KCl-LiCl eutectic system flux

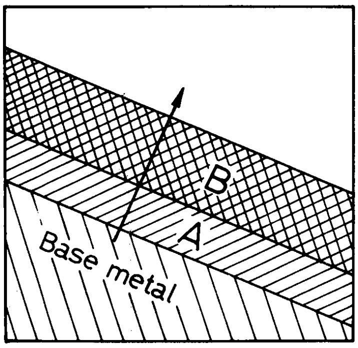
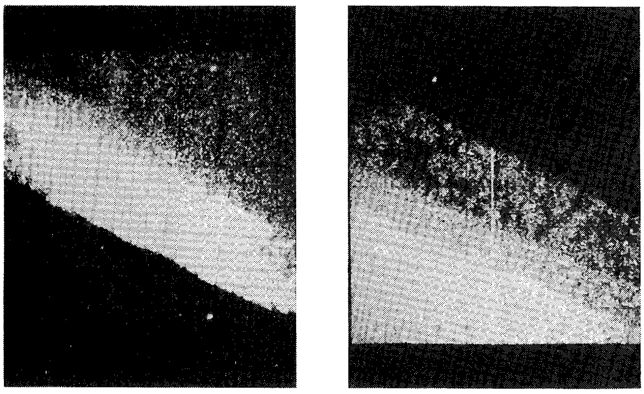


Fig. 3 Schematic explanation of cross section at the interface

section of two layers at the interface of spread specimen. Moreover, in Photo. 1, characteristic X-ray images of Ag-Lα and Cu-Kα at the interface are shown.



a) AgL_{α} b) CuK_{α}

Photo. 1 Characteristic X-ray images at the interface between spread metal and base plate

3-1-3 Comparison of the compositions of alloys after spreading test with commercial BAg filler matals

To compare the compositions of alloys after spreading test with commercial BAg filler metals, line analysis results of Ag, Cu and Zn in BAg filler metals after spreading test on copper plate with KCl-LiCl eutectic flux are shown in Figs. 4 and 5, respectively for BAg-1 and BAg-3, and those results are listed in Table 6, together with results of BAg-5 and BAg-7. When we compare the compositions of the used solder after spreading test with the compositions shown in Table 6, the compositions of the spread solder which contains 41wt%Ag shown in Table 5 approximately coincidence with that of BAg-1 shown in Table 6. Moreover, this experimental fact is assured also from the similarity of both results of Figs. 2 and 4.

Table 6 Compositions of BAg filler metals spread on Cu plate using KCl–LiCl eutectic flux

Type	Test temp. (°C)	Approximate composition by EPMA(wt%)					
		Ag	Cu	Zn	Cd	Sn	Ni
BAg-1	700	42	22	12	24	–	–
BAg-3	760	39	31	10	18	–	3
BAg-5	820	44	40	16	–	–	–
BAg-7	760	50	33	12	–	5	–

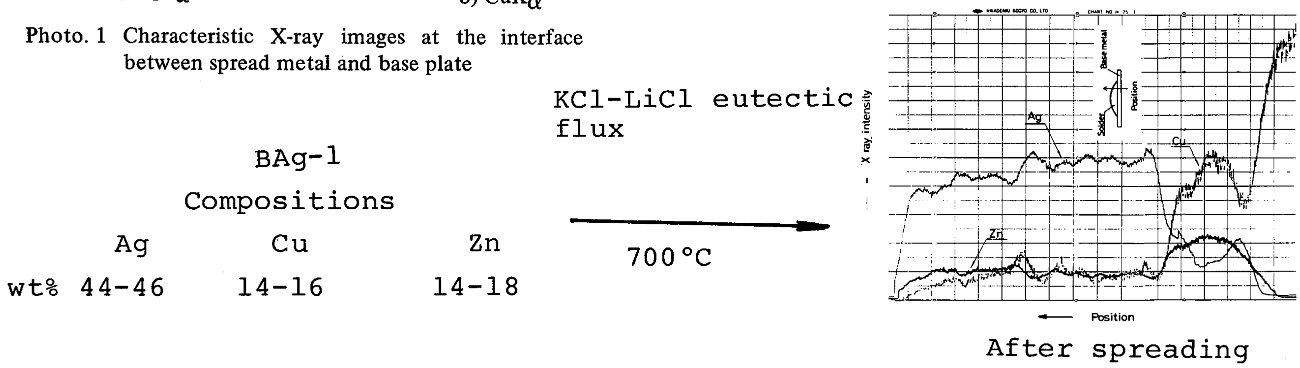


Fig. 4 Distributions of Ag, Cu and Zn in the case of BAg-1 spread on Cu plate

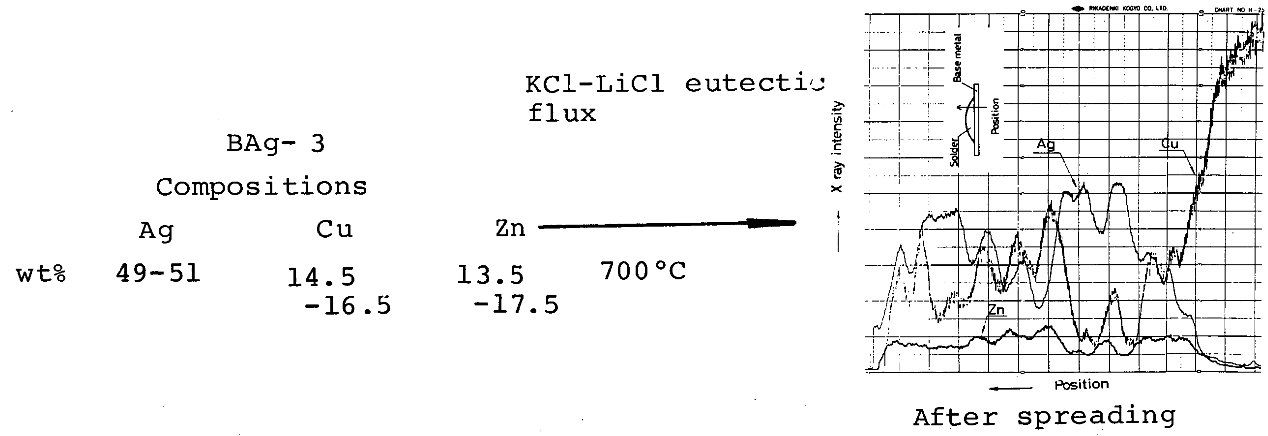


Fig. 5 Distributions of Ag, Cu and Zn in the case of BAg-3 spread on Cu plate

3.2 Factors controlling the dissolution of silver into Zn-Cd binary alloys

As shown in Tables 4 and 5, the content of copper, which is the component of base plate, in spread metal increases with raising of heating temperature and the dissolved copper forms brass of about 45wt%Zn at the domain of A, so that the dissolution action of silver from the used flux into the solder is considerably affected. Therefore, pure nickel plate was used as base plate to remove the dissolution of the component of base plate. In this case, the dissolving of nickel into Zn-Cd alloys after spreading test is not almost acknowledged.

From the results of 58wt%Zn-42wt%Cd and 77wt%Zn-23wt%Cd alloys, it is noticed that the higher heating temperature becomes, the more the dissolution amount of silver becomes. However, the amount of zinc in alloys after spreading test remarkably decreases than that of the alloys before spreading test, but is not almost diminished for cadmium of solder component. In the case of 14wt%Zn-86wt%Cd alloy, as Ag_3PO_4 reacts with both metals of zinc and cadmium, the amount of zinc in the spread metal is comparatively small. However, the silver salt chiefly reacts with zinc, which is more base than cadmium, according to the decrease of cadmium content in the solder. Moreover, a Zn-Cu alloy or Zn-Ni alloy layer is formed at the interface between the spread metal and base metal, according as zinc content in the solder increases. The formation of the layer is remarkably seen with upward tendency of test temperature. And, the Zn-Cu layer or the Zn-Ni layer is greatly formed in the case of 58wt%Zn-42wt%Cd alloy or 77wt%Zn-23wt%Cd alloy, because zinc in the alloy used as solder has strong affinity with copper or nickel of base plate than cadmium of solder.

When the spread metal of similar compositions as BAg-1 filler metal was obtained, the formation mechanism may be due to the following process; copper of base plate dissolves into the molten solder and, when the specimen is cooled, the primary crystal of Cu-Zn alloy at first crystalizes at interface between the spread metal and the base metal. On the other hand, Ag of Ag_3PO_4 used as flux dissolves into the molten solder by mutual dissolution action, and the formation of Ag-Cd layer is considered as described already in 3-1-1. Accordingly, the composition of spread metal is controlled by cooling condition of a quasi Ag/Cd alloy-Cu/Zn alloy binary system. As shown in Fig. 2, the distributions of alloy elements at left side, which is the top surface part of spread metal, are like the eutectic constituent of this quasi binaly system, whereas the distributions of right side correspond to the primary crystal of Cu-Zn alloy. The amount of silver dissolved at the top surface part of spread metal, then, may be controlled by the solubility of copper into molten solder and the content of primary crystal of Cu-Zn alloy. Namely, it is expected that the more the content of primary crystal becomes, the less the content of silver becomes. In this experiment, as shown in the column of 600°C in Table 5, the value of silver was 41wt%, and the spreading time is 2 min.

3.3 Dissolution of nickel or copper from flux into various alloys

In above sections, the dissolution of silver from silver salt into molten Zn-Cd alloys was investigated and, it was confirmed that a great amount of silver dissolved in molten 77wt%Zn-23wt%Cd alloy to give the spread metal of similar compositions as BAg filler metal. However, copper of base metal dissolved in the spread metal. In this section, to know whether the dissolution of copper or nickel from flux is possible, the same spreading tests were done at 500°C with $CuCl_2$ or $NiCl_2$ as flux. The results are shown in Table 7. The copper dissolved in the molten solder is less amount in the case of $SnCl_2$ base flux than that of KCl-LiCl eutectic base flux. However, the dissolution amount of copper or nickel is about 15wt%. This value approximately agrees with the solubility of copper in molten tin at 500°C. From this agreement, the solution rate of copper to tin is believed to be considerably fast, because the heating time is 2 min. Accordingly, the copper content which corresponds to BAg filler metal may be easily obtained from copper base salt into the Sn-Zn or Zn-Cd solder alloys.

Table 7 Compositions of solders spread on nickel plate with various

Flux	Alloy	Approximate composition by EPMA(wt%)				
		Cu	Sn	Ni	Zn	Cd
20mol% $CuCl_2-SnCl_2$	Sn	10	86	4	–	–
	84Sn–16Zn	11	86	3	no detect	–
	86Cd–14Zn	5	87	1	no detect	–
20wt% $CuCl_2$–(KCl* LiCl)	Sn	17	81	2	–	–
	84Sn–16Zn	17	82	1	no detect	–
	86Cd–14Zn	13	–	6	5	76
20wt% $NiCl_2$–(KCl* LiCl)	Sn	24	65	11	–	–
	84Sn–16Zn	5	79	16	no detect	
	86Cd–14Zn	7	–	8	5	80

* KCl–LiCl eutectic salt

4. Conclusion

The dissolution of silver, copper or nickel from flux into Zn-Cd alloys used in spreading test on copper or nickel base plate was investigated. The results obtained are summarized as follows;

1) When the 77wt%Zn-23wt%Cd alloy as solder and the 30wt/Ag_3PO_4/LiCl-KCl system eutectic salt as mixed flux are used in spreading test on copper base plate at 600°C for 2 min., the compositions of spread metal are similar to the composiitons of BAg-1 filler metal spread on copper base plate at 700°C. Accordingly, the depression of 100°C of a recommended brazing temperature will be achieved by this proposed method in silver brazing.
2) Although the reactions occuring in between Ag_3PO_4 used as mixed flux and Zn-Cd alloy used as solder are promoted with increasing the temperature, the content of dissolved silver in metal spread on copper base plate decreases owing to the dissolution of base plate component.
3) It was found in spreading test on nickel base plate at 500°C that the copper content in pure tin or 84wt%Sn-16wt%Zn alloy used as solder approximately agrees with the solubility of copper in Cu-Sn binaly system diagram when 20wt%$CuCl_2$ is contained in the used flux. From this result, the solution rate of copper into molten tin was considered to be very fast. In fact, it is already well known in soldering of copper that η (about 59wt%Sn) or ϵ (about 38wt%Sn) phase is formed within shorter time and at soldering temperature of about 350°C which is lower than that used in our experiment.

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