Studies on Flux Action of Soldering (Report VI)†
—Effect of Metal Salts on Dissolution of Zn in Molten Sn—

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Abstract

In flux action of soldering, it is acknowledged that various metal salts react with molten Sn solder and metal is dissolved into Sn from metal salts. In soldering, the dissolution of metal into solder from base plate is noticed as remarkable at high temperature.

In this report, authors have discussed the various effects of dissolution of Zn into molten Sn solder by dissolving metals produced by the reaction of Sn with various metal salts into Sn.

The results obtained from this investigation are as follows.

1) *When metal sulfates such as Ag_2SO_4, $CuSO_4$, $CoSO_4$ and $NiSO_4$ were used as flux, the dissolution of Zn from metal in molten Sn was accelerated by the dissolution of metals (Ag, Cu, Co and Ni) in Sn from metal sulfates, and Ag-Zn, Cu-Zn, Co-Zn and Ni-Zn layers were formed in Sn solder.*
2) *In the case of $Bi_2(SO_4)_3$ and $PbSO_4$, the dissolution of Zn into molten Sn is not affected much by the dissolution of Bi or Pb.*
3) *Effect of the dissolution of metals from various metal sulfates on the dissolution of Zn into molten Sn may be considered on the basis of the heat (ΔH) of formation of alloy between metal and Zn.*

1. Introduction

In the flux action of soldering, it has been noticed that various metal salts react with Sn solder and metal is dissolved in Sn from metal salt by the reaction[1), 2)]. The dissolution of metal to solder from base metal may play an important role in soldering, and is formed well at high temperature.

In this report, it was studied whether the dissolution of Zn into Sn solder from Zn plate is affected by the dissolution of various metals in Sn from the flux by the reaction of various metal salts with molten Sn or not. And, moreover the dissolution of Zn into Sn-Metal alloy was investigated in order to know the variation of the dissolution of Zn by metal added to Sn. The dissolution of Zn in Sn solder was elucidated by analyzing the cross section of test specimens by EPMA. Effect of dissolution in molten Sn by metal was teken into the consideration of the thermal kinetics. (ΔH values)

2. Experimental Procedure

Commercially available reagent-grade $C_6H_5NH_2\cdot HCl$ and various metal salts were used as flux in this experiment after drying.

In carring out these tests, Zn plates (40×40×0.4 m/m, 99.9%) were polished with 06# emery paper and grease and dust were removed by washing with acetone just before the testing.

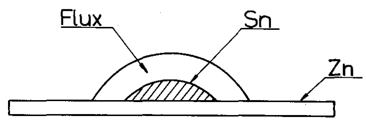

Fig. 1. Test specimen for dissolution of Zn in Sn with various fluxes.

As shown in **Fig. 1,** Sn (100mg) and flux (100mg) were placed in the center of Zn plate on a hot plate at a controlled temperature. The specimens were heated to required temperature (250°C) and maintained for 45 sec, and then removed and cooled. The dissolution of Zn and metal from flux in Sn was elucidated by EPMA.

3. Results and Discussions

3.1 The effect of metal sulfates on dissolution of Zn in molten Sn

In order to know the effect of various metal sulfates on the dissolution of Zn into molten Sn, the dissolution of Zn into molten Sn was studied the first of all at 250°C for 45 sec as shown in Fig. 1 with using only $C_6H_5NH_2\cdot HCl$ as flux.

Fig. 2 shows typical dissolution state of Zn into Sn in the case of $C_6H_5NH_2\cdot HCl$ flux. The amount of

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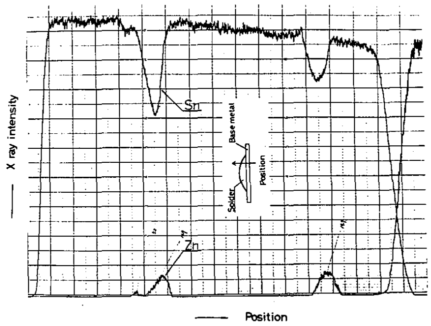

Fig. 2. X-ray micro-analysis of Sn and Zn of cross section of test specimen with $C_6H_5NH_2 \cdot HCl$.

Zn dissolved into Sn from base metal (Zn) is small and the dissolution of Zn is found at the interfacial surface between molten Sn and Zn. And in order to elucidate the effect of various metal sulfates, the dissolution of Zn into molten Sn with using $C_6H_5NH_2 \cdot$ HCl- metal sulfate system flux was compaired with the dissolution in the case of only $C_6H_5NH_2 \cdot HCl$ flux. The experiment for dissolution of Zn was done at 250°C for 45 sec. as shown in Fig. 1 with using 90mol%$C_6H_5NH_2 \cdot HCl$-10mol% metal sulfate system flux. Inspectered results by EPM analysis of cross section of test specimens were shown in **Fig. 3 ~ Fig. 6** respectively for Ag_2SO_4, $CuSO_4$, $CoSO_4$ and $NiSO_4$.

From Fig. 3, in the case of Ag_2SO_4, the dissolution of Zn in all the part of Sn solder was remarkable noticed in contrast to the case of $C_6H_5NH_2 \cdot HCl$ only flux, and a great amount of Ag from Ag_2SO_4 is co-existed with Zn in all the part when Zn from base metal is dissolved in Sn. We note that Ag-Zn phases are formed in Sn solder.

As shown in Fig. 4 and Fig. 5, when 10mol% $CuSO_4$ or 10mol % $CoSO_4$ added to $C_6H_5NH_2 \cdot HCl$ the amount of dissolution of Zn in Sn is further increased than in the case of 100 % $C_6H_5NH_2 \cdot HCl$.

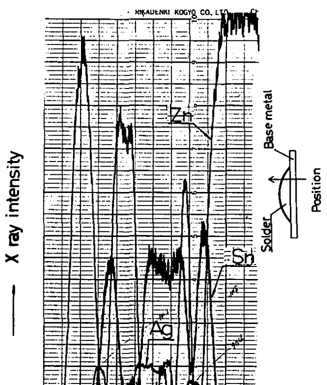

Fig. 3. X-ray micro-analysis of Sn, Zn and Ag of cross section of test specimen with Ag_2SO_4.

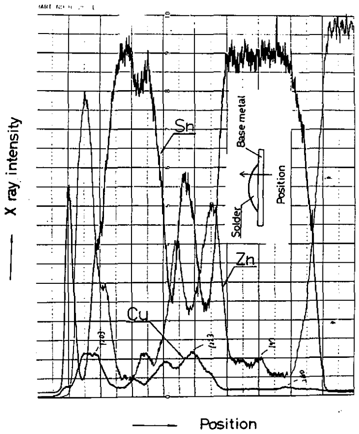

Fig. 4. X-ray micro-analysis of Sn, Zn and Cu of cross section of test specimen with $CuSO_4$.

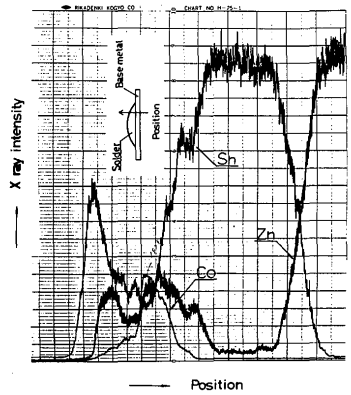

Fig. 5. X-ray micro-analysis of Sn, Zn and Co of cross section of test specimen with $CoSO_4$.

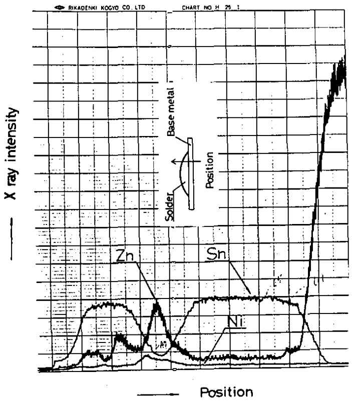

Fig. 6. X-ray micro-analysis of Sn, Zn and Ni of cross section of test specimen with $NiSO_4$.

And Cu or Co co-existed with Zn and Cu-Zn phases or Co-Zn phases are formed in Sn solder like as in the case of Ag_2SO_4.

From Fig. 6, in the case of $NiSO_4$, a small amount of Ni are dissolved in Sn, however, the dissolution of Zn in Sn is increased by the dissolution of Ni and it is recognized that Zn-Ni phases are formed.

When the flux action of $Bi_2(SO_4)_3$ is considered, the dissolution of Zn in Sn is about similar to that of the case of $C_6H_5NH_2 \cdot HCl$ only flux as shown in Fig. 2

though it is noticed that amound of Bi is dissolved in Sn solder uniformly by the reaction of $Bi_2(SO_4)_3$ with molten Sn. The dissolution Bi into Sn solder does not affect the dissolution of Zn in Sn. The result of EPM analysis in the case of $Bi_2(SO_4)_3$ is shown in **Fig. 7.**

The flux action of $PbSO_4$ is similar to that of $Bi_2(SO_4)_3$. Amount of Pb is dissolved uniformly in Sn, but the dissolution does not effect much on increasing the dissolution of Zn in Sn from base metal. The result of EPM analysis is shown in **Fig. 8.**

Table 1 summarizes above results for the effect of various metal sulfates on the dissolution of Zn. For the formation of metal compounds between metal from flux and Zn from base metal, the effect of various metal sulfates on the dissolution of Zn from base metal is classified roughly in two (Table 1). Namely, in the case of metal sulfates such as Bi and Pb, these metal sulfates have not influence much on the dissolution of Zn from base metal though these metal from metal sulfates dissolve uniformly in Sn solder.

And, in the case of metal sulfates such as Ag, Cu, Co and Ni, the dissolution of Zn from base metal is promoted by the dissolution of metals (Ag, Cu, Co and Ni) produced by the reaction of metal sulfate with molten Sn. Then, Metal-Zn phases are formed at the area where Zn exists in Sn that is, Zn-Ag, Zn-Cu, Zn-Co and Zn-Ni compounds are formed.

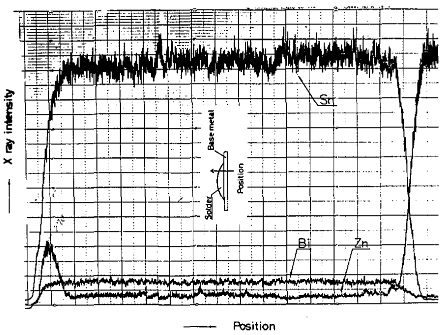

Fig. 7. X-ray micro-analysis of Sn, Zn and Bi of cross section of test specimen with $Bi_2(SO_4)_3$.

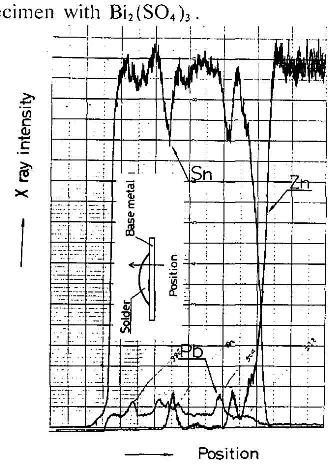

Fig. 8. X-ray micro-analysis of Sn, Zn and Pb of cross section of test specimen with $PbSO_4$.

3.2 Effect of various metals on the dissolution of Zn in Sn-Metal alloy

In section 3-1, the effect of the dissolution of metal from flux on the dissolution of Zn, from base metal in Sn was cralified. In this section, the effect of metals on the dissolution of Zn in various Sn-Metal (Ag, Bi, Pb and Cd) alloys was investigated using $C_6H_5NH_2 \cdot HCl$ only flux as shown in **Fig. 9** in comparison with the dissolution of Zn in Sn.

Results of EPM analysis of tests done at 250°C for 45 sec with using various Sn-Metal alloy and $C_6H_5NH_2 \cdot HCl$ flux are shown in **Fig. 10**～ **Fig. 12** respectively for Sn-5Ag alloy, Sn-Bi and Sn-Pb eutectic alloy. From above results, metals such as Bi and Pb do not dissolve much into base metal and depress the dissolution of Zn into Sn solder. However, when Sn-5% Ag alloy is used, Ag promotes the dissolution of Zn into Sn solder and Zn-Ag layers are formed in

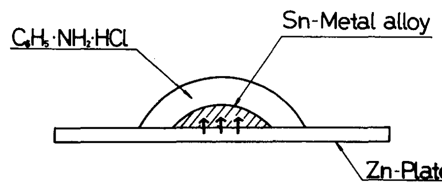

Fig. 9. Test specimen for dissolution of Zn in Sn-Metal alloy.

Table 1. Dissolution of Zn in Sn with various metal sulfate fluxes and formation of Metal-Zn layer.

	Various sulfates	Metal dissolution from flux	Dissolution of Zn	Formation of Metal-Zn phase
A	$PbSO_4$	○	Small	×
	$Bi_2(SO_4)_3$	○	Small	×
B	Ag_2SO_4	○	large	○
	$CuSO_4$	○	large	○
	$CoSO_4$	○	large	○
	$NiSO_4$	○	large	○
C	$C_6H_5NH_2 \cdot HCl$	×	Small	×

○.... recognized ×.... not recognized

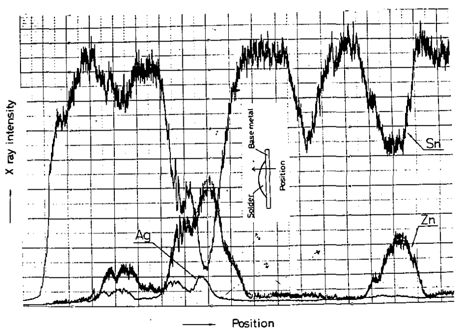

Fig. 10. X-ray micro-analysis of Sn, Zn and Ag of cross section of test specimen with $C_6H_5NH_2 \cdot HCl$.

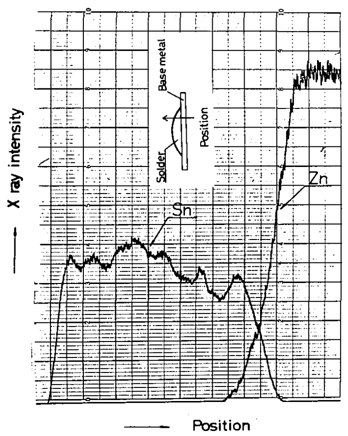

Fig. 11. X-ray micro-analysis of Sn and Zn of cross section of test specimen with $C_6H_5NH_2 \cdot HCl$.

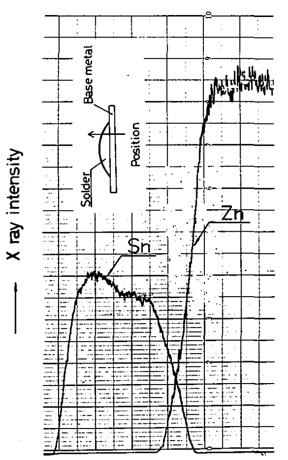

Fig. 12. X-ray micro-analysis of Sn and Zn of cross section of test specimen with $C_6H_5NH_2 \cdot HCl$.

solder. Ag added in Sn showed the similar effect as Ag from Ag_2SO_4 by the reaction of molten Sn, though the effect of Ag in Sn-5%Ag alloy is not so much great as one of Ag from Ag_2SO_4. Namely, it is acknowledged that Pb and Bi in solder do not play an important role in the dissolution of Zn into solder like as Pb and Bi from $PbSO_4$ and $Bi_2(SO_4)_3$. However, Ag in solder effects well on the dissolution of Zn in solder like as Ag from Ag_2SO_4.

3.3 Action of metal on the dissolution of Zn into solder

From the results in above sections, various metal sulfates showed the different flux action for dissolving of Zn into molten Sn. Metal such as Ag, Cu, Ni and Co in Sn from sulfates promoted the dissolution of Zn from base metal. However, the dissolution of Zn were not accelerated much by the dissolution of Bi and Pb form flux in Sn. Effects of metal on dissoltion of Zn into molten Sn with respects to metal sulfates (Ag, Cu and etc) are considered as follows.

The first of all, it may be necessary that the reaction (eq-1) between molten Sn and metal sulfate comes about at the surface of solder and metal from sulfate dissolves into Sn solder as shown in **Fig. 13 (a)** and **(b).**

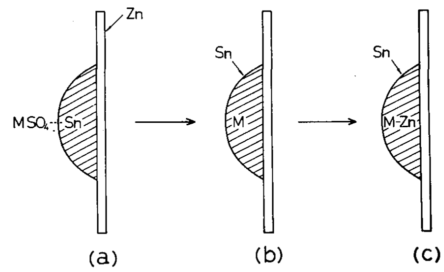

Fig. 13. Diagram of path of dissolution of Zn in Sn.

$$MSO_4 + Sn \longrightarrow SnSO_4 + M \quad \text{------------------------} (1)$$

Then, metal dissolved in molten Sn contacts easily with Zn which dissolves in Sn at the interfacial layer between molten Sn and Zn (base metal) as shown in **Fig. 13 (c).** So, metal bonds to Zn and Metal-Zn alloys of higher melting point than 250°C is formed in Sn. It may be considered that above reaction in Sn is repeated and the dissolution of Zn into Sn is enhanced only when metal contacts easily with Zn. So, the reaction of metal with Zn in molten Sn was taken into consideration on the basis of the heat (ΔH)[3] of formation of alloy between metal as shown in **Table 2.** Namely, it is considered that the formation of alloy between metal and Zn is easy when the values of ΔH is large in minus sign. However, the formation of alloy is difficult when values of ΔH were large in plus sign.

Table 3 shows the easiness of the formation of alloy between two metals on the basis of the values of ΔH as shown in Table 2. From Table 3, Ag and Cu may react easily with Zn in comparison with Sn, and Ag-Zn and Cu-Zn alloy may be formed easily. So, it may be considered that the dissolution of Zn

Table 2. Values of ΔH for alloying between two metals.

Metal A-Metal B	Temp °C	Value of ΔH	Atom fraction
Zn-Ag	427	−1150	0.5
Zn-Cu	—	−2185β	0.5
Zn-Sn	430	792	0.5
Zn-Bi	—	1080	0.5
Zn-Pb	653	1800	0.5
Ag-Sn	450	−210	0.6
Bi-Sn	—	24	0.5
Cu-Sn	1200	−880	0.3
Pb-Sn	450	330	0.5

Table 3. Easiness of combination among Zn-Metal-Sn (Ag, Cu, Bi and Pb).

	Metal-metal	Easiness of Combination
Ag	Sn-Zn	×
	Ag-Zn	◎
	Ag-Sn	○
Cu	Sn-Cu	○
	Cu-Zn	◎
	Sn-Zn	×
Pb	Sn-Pb	×
	Pb-Zn	×
	Sn-Zn	×
Bi	Sn-Bi	○
	Bi-Zn	×
	Sn-Zn	×

×···· Difficult ○···· Easy to combination
◎···· The easiest to combination

into molten Sn is enhanced by the dissolution of Ag or Cu in the case of Ag_2SO_4 and $CuSO_4$. However, Pb and Bi does not react easily with Zn and the formation of Pb-Zn or Bi-Zn alloy may not be noticed. So the dissolution of Zn into molten Sn in the case of $PbSO_4$ or $Bi_2(SO_4)_3$ shows a similar results as the dissolution of Sn in the case of 100% $C_6H_5NH_2 \cdot HCl$ flux. In the case of $CoSO_4$ and $NiSO_4$, it may be considered that Co and Ni react with Zn in Sn and the formation of Co-Zn alloy and Ni-Zn alloy induces the increase of the dissolution of Zn into Sn. Ag in Sn-5% Ag alloy, too, may induce the dissolution of Zn into Sn like as Ag from Ag_2SO_4.

4. Conclusion

Effects of the dissolution of metals produced by the reaction of molten Sn with various metal sulfates on the dissolution of Zn from base metal in molten Sn were investigated.

From this experiment, following results were clarified.

1) When metal sulfates such as Ag_2SO_4, $CuSO_4$, $CoSO_4$ and $NiSO_4$ were used as flux, the dissolution of Zn from base metal in molten Sn was enhanced by the dissolution of metals (Ag, Cu, Co and Ni) in Sn from metal sulfates, and Ag-Zn, Cu-Zn, Co-Zn and Ni-Zn compounds were formed in Sn solder.

2) In the case of $Bi_2(SO_4)_3$ and $PbSO_4$, the dissolution of Zn into molten Sn is not affected much by the dissolution of Bi or Pb.

3) Effect of the dissolution of metals from various metal sulfates on the dissolution of Zn into molten Sn may be explained on the basis of the heat (ΔH) of formation of alloy between metal and Zn.

Acknowledgement

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