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Studies on Flux Action of Soldering (Report IV)[†]
—Inorganic Metal Salts—

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Abstract

In previous papers on aniline hydrochloride flux action of soldering, it has been shown that molten aniline hydrochloride reacts with copper to give $CuCl_2$ and copper complex, which react with molten solder of Sn-Pb alloy to give metallic copper. Successively this copper dissolves into the molten solder and a thin Cu-rich layer is formed on the surface of molten solder. The wetting of copper plate by the solder is improved through the reaction and the dissolution of Cu into molten solder.

In this report, the flux action of various inorganic metal salts (chloride, sulfate and nitrate) on soldering was studied in the relation between the reaction of flux with Sn and wettability of solder on Cu plate.

The flux action of various inorganic metal salts may be considered as follows; The reaction of molten Sn with metal salt is mainly controlled to electrochemical series of metal in molten salt. The effect of metal salt on spreading is dependent mainly on the electrochemical series, and the improvement of spreading by inorganic salts may be ascribed to the reaction of molten Sn with metal salt and the dissolution of the metal into molten Sn from flux.

The difference in effect on spreading by inorganic metal salts is acknowledged to some degree.

1. Introduction

The flux for soldering is mainly used experiencely, and these fluxes are classified to organic acids represented by rosin, organic amine such as $C_6H_5NH_2 \cdot HCl$, inorganic metal salts and inorganic acids. The improvement for spread with these fluxes has been reportedly attributed to be the elimination[1] of oxides on base metal or electro-chemical action[2].

Recently, we have reported on the stearic acid flux action[3, 4] of soldering as follows;

$$CuO + 2C_{17}H_{35}COOH \xrightarrow{\triangle} Cu(O\overset{O}{\overset{\|}{C}}C_{17}H_{35})_2 + H_2O \text{ ----- } (1)$$

$$Cu(O\overset{O}{\overset{\|}{C}}C_{17}H_{35})_2 + Sn-Pb \text{ alloy} \xrightarrow{\triangle} 2C_{17}H_{35}COOH + Cu-(Sn-Pb \text{ alloy}) \quad (2)$$

Molten stearic acid reacts with copper oxide to give clear copper surface and copper stearate which reacts with molten Sn-Pb eutectic alloy solder to give metal Cu, as shown in eq. (1) and eq. (2). The Cu dissolves into solder, and solder spreads over Cu plate to improve wettability of solder on Cu plate. And moreover, the relation between the reaction of Cu-stearate with solder and spread area with Cu-stearate flux was applied to other metal stearate[5, 6]. Then, $CuCl_2$ is produced by the reaction of eq. (3) when $C_6H_5NH_2 \cdot HCl$ is used as flux[7, 8], and it was pointed out that reaction between the Cu salt and molten Sn (eq. (4)) or dissolution of Cu into Sn is important factor controlling flow and spread.

$$Cu + 2C_6H_5NH_2 \cdot HCl \xrightarrow{\triangle} CuCl_2 + 2C_6H_5NH_2 + H_2 \text{ --- } (3)$$

$$2CuCl_2 + Sn \xrightarrow{\triangle} SnCl_4 + 2Cu-(Sn) \text{ -------------------- } (4)$$

In this report, we wish to report the chemical phenomenon of soldering and the relation between flux action of inorganic metal salts and spreadability of Sn solder on copper plate in comparison with the results in the case of stearic acid flux and aniline hydrochloride flux. So, the reaction of Sn solder with inorganic metal salts (chloride, sulfate and nitrate) and the spreadability of Sn solder on copper plate with these flux were studied on the basis of electrochemical series of metal in molten salts.

2. Experimental procedure

Commercially available reagent-grade $C_6H_5NH_2 \cdot HCl$, various metal halides, metal sulfates and metal nitrates were used as flux in this spreading test after drying. JIS—CuP copper plate (40×40×0.4mm) electropolished was used as base metal, and Sn (99.999%) is used as solder. The similar method as described in the earlier paper[8] was adopted in

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spreading test and the amounts of flux and solder are 0.1g respectively. The dissolution in Sn solder of metal produced by reaction between various inorganic metal salts and molten Sn was elucidated by analizing the cross section of specimens after spreading test by EMX analyzer.

3. Results and Discussions

3.1 The effect of various metal chlorides on spreadability

In the earlier papers[7, 8], the effect of $CuCl_2$ on wettability of Sn solder on Cu plate was explained. Accordingly, flux action for wettability of various chlorides of metal such as Zn, Fe, Ni, Pb and Ag to Sn solder on Cu pate was investigated by using $C_6H_5NH_2$-metal chloride system flux with different compositions. The spreading test with these fluxes was tried under similar conditions as described in earlier paper[6]. And the results are shown in **Fig. 1** and **Fig. 2.**

As shown in figures, the effect to wettability of

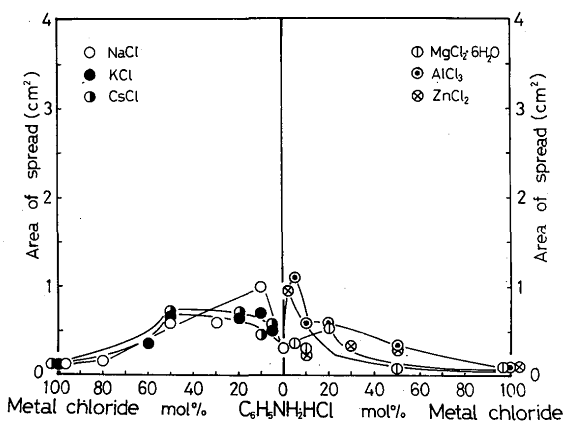

Fig. 1. Spreading of Sn solder on copper plate with $C_6H_5NH_2 \cdot HCl/MCl_n$ flux at 250℃.

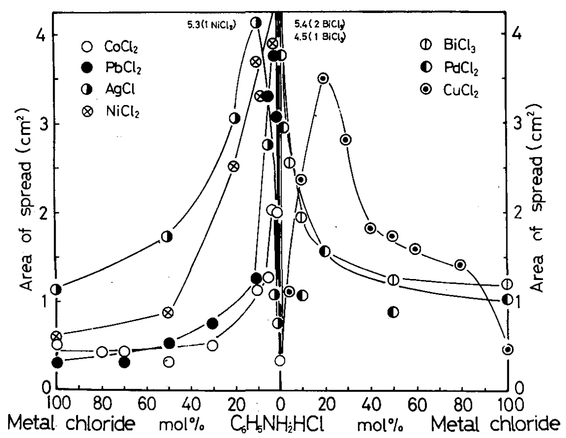

Fig. 2. Spreading of Sn solder on copper plate with $C_6H_5NH_2 \cdot HCl_n$ flux at 250℃.

metal chloride in the case of addition of metal chloride of high ionization tendency isn't achnowledged. And as shown in the figures, in the case of the chlorides flux of metals (Na, Zn, Al etc.) which are the first members of the electrochemical series, the difference of spread area isn't acknowledged remarkably in comparison with in the case of only $C_6H_5NH_2 \cdot HCl$ flux (Fig. 1). However, in the case of the chlorides of metals (Ag, Cu etc.) which are the last members of series, the addition of a some portion of these chlorides to $C_6H_5NH_2 \cdot HCl$ has a great effect on the improvement of spreading (Fig. 2).

As it is cleared that reaction between solder and metal salt or dissolution of metal from flux into solder are primary factor controlling spread in the earlied paper[8], the cross section of specimens after spreading using various metal chloride fluxes was analyzed by EMX analyzer owing to persue the cause of the differences in spreading by sort of metal when various metal chlorides were used as flux.

The results are shown in **Fig. 3, Fig. 4, Fig. 5** and **Fig. 6** respectively for $ZnCl_2$, $AlCl_3$, $NiCl_2$, and AgCl. As shown in the results of EMX analysis, it was recognized that metal from chloride flux such as Mg, Zn, Al etc. dissolved scarcely into Sn solder. Nevertheless, it is observed that the various metals dissolve into Sn solder by the reaction of Sn solder with metal chloride flux such as Pb, Ni, Ag and Bi whose large effect on wettability is acknowledged. The reaction of molten Sn with various metal chlorides (eq. (5)) may play important role in spreading of Sn solder on Cu plate in the case of various metal chlorides.

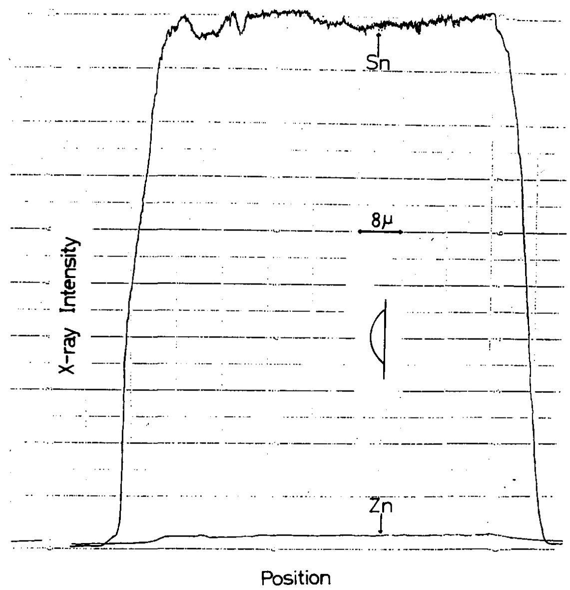

Fig. 3. X-ray micro-analysis of Zn and Sn of cross section of Sn solder spread on copper plate with $ZnCl_2$.

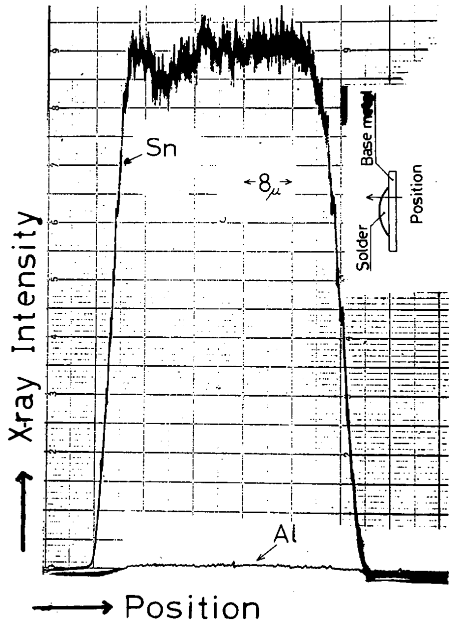

Fig. 4. X-ray micro-analysis of Al and Sn of cross section of Sn solder spread on copper plate with $AlCl_3$.

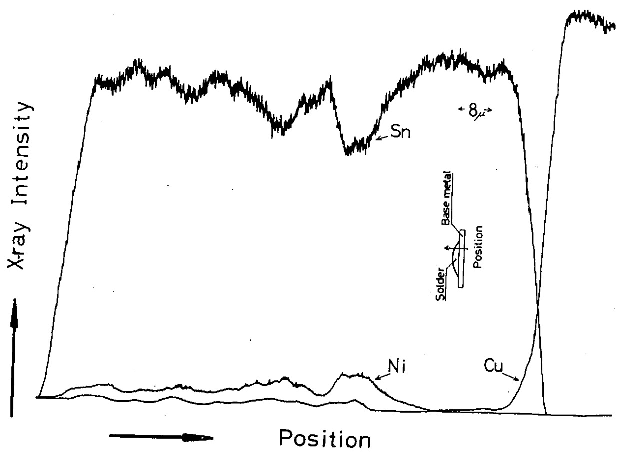

Fig. 5. X-ray micro-analysis of Ni, Cu and Sn of cross section of solder spread on copper plate with $NiCl_2$.

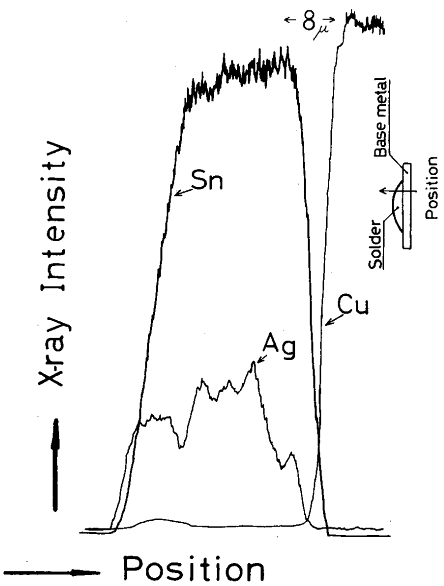

Fig. 6. X-ray micro-analysis or Ag, Cu and Sn of cross section of Sn solder spread on copper plate with AgCl.

$$MCl_n + \frac{n}{2} Sn \xrightarrow{\triangle} \frac{n}{2} Sn\ Cl_2 + M \text{ ----------------------- (5)}$$

The reaction between metal (Sn) and metal chloride is considered on the basis of thermal kinetic (normal free energy) and electrochemical sereies of metal (oxidation and reduction potential). In this report, the reaction was taken in consideration on the basis of the electrochemical series of metal. The first of all, for aqueous solution, the electrochemical series is formed on the basis of the value of standard electrode potentials and is shown as follows;

K, Ca, Cs, Na, Mg, Al, Zn, Fe, Co, Ni, [Sn], Pb, H, Cu, Ag, Pd, Au

When the reaction (eq-(5)) is considered on the basis of the electrochemical series for aqueous solution, the reaction of Sn with metal chloride may proceed, since the metals (Pb, Cu, Ag, Pd) are more noble than Sn. In the case of Co and Ni, the reaction may not proceed on the basis of the electrochemical series, because these metals are more base than Sn. However, these metal halides react with Sn solder and the effect of these fluxes ($CoCl_2$, $NiCl_2$) on spreading was recognized in this experiment. Thereupon, satisfactory answer to Co and Ni isn't gained. In the case of various metal stearates, in the earlier paper[5, 6] the reaction with solder and spread area shows fixed quantative relation. So, in the case of metal chloride, the spread area may be considered to depend on the reacting of Sn with metal chloride. And, the electrochemical series were set up on the basis of the maximum values of spread area and the results of EMX analysis as follows;

[Sn], Co, Cu, Pd, Pb, Ag, Ni, Bi

And it may be considered that Na, K, Al, Cs and Zn etc. are more base than Sn as the chlorides of these metals are uneffective to spreading and do not react with Sn solder. Neverthless, the series of these metals isn't clear from spread area. Practically, it is shown that electrochemical series are different in solvent[9]. Though the solvent in this test is $C_6H_5NH_2 \cdot HCl$, the electrochemical series in its solvent was not set up. So, electrochemical series[9] at 500℃ in chloride system (NaCl-$AlCl_3$) which is comparatively similar system to this experiment is given as follows;

→ base noble →
Na, K, Al, Zn, Cd, [Sn], Pb, Co, Ag, Cu, Bi, Ni

Accordingly, though there is a some difference of order in comparing electrochemical series obtained from spread area with the series in NaCl-$AlCl_3$, Na, K, Al and Zn are more base than Sn in two series and Pb, Co, Ag, Cu, Bi and Ni are nobler than Sn. The last members of these two series are mainly Cu, Bi, Ni and two series are very similar.

From results, it was ascertained that electrochemical series of metal, namely, the reaction between Sn and metal chloride results in important factor controlling spread of Sn solder on Cu plate.

3.2 The effect of various metal sulfates on spreading

In clause 3.1, the effect on various metal chlorides on spreading was proved. In this section, spreading test of Sn solder on Cu plate was done under the same condition against foregoing paragraph in order to clear the effects of metal or SO_4 group in metal sulfate on spreading in comparison with metal chlorides. The results are shown in **Fig. 7** and **Fig. 8.**

As shown in figures, the effect of addition of sulfate of metal which is comparatively base is scarcely recognized as well as that of metal chlorides, and the spread areas showed similar values in comparison with in the case of only $C_6H_5NH_2HCl$ flux. Nevertheless, the effect of addition of sulfate of metal which is comparatively noble is acknowledged and and spread area increases remarkably.

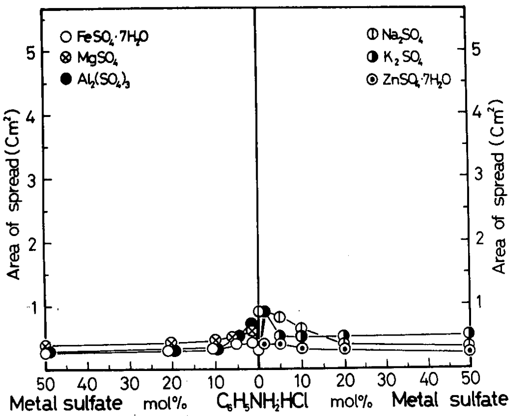

Fig. 7 Spreading of Sn solder on copper plate with $C_6H_5NH_2HCl$ $/M_n(SO_4)_m$ flux at 250°C.

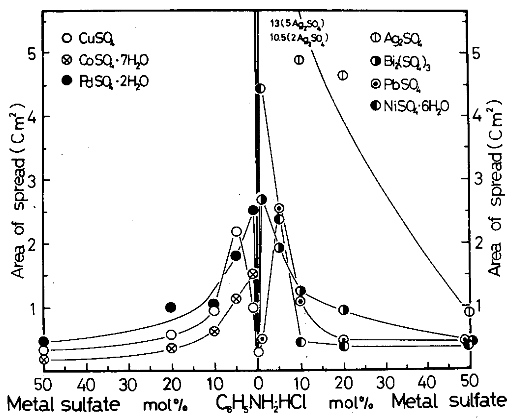

Fig. 8. Spreading of Sn solder on copper plate with $C_6H_5NH_2HCl$ $/M_n(SO_4)_m$ flux at 250°C.

In order to clear the reaction between molten Sn and metal sulfate, the cross section of specimen after spreading test was analyzed by EMX analyzer. The results are shown in **Fig. 9, 10** and **11.** From the results of EMX analysis, the effect of spreading was acknowledged in the case of sulfate salt of metal such as Ag, Bi, Ni, Pb, Pd, Cu and Co which dissolves into Sn solder respectively. Accordingly, electrochemical series of sulfate was set up on basis of maximum values of spread area and the results of EMX analysis as follows;

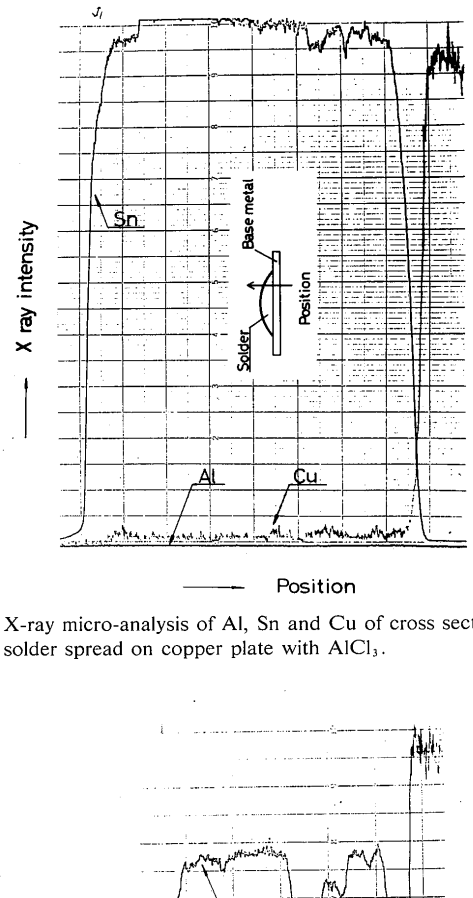

Fig. 9. X-ray micro-analysis of Al, Sn and Cu of cross section of Sn solder spread on copper plate with $AlCl_3$.

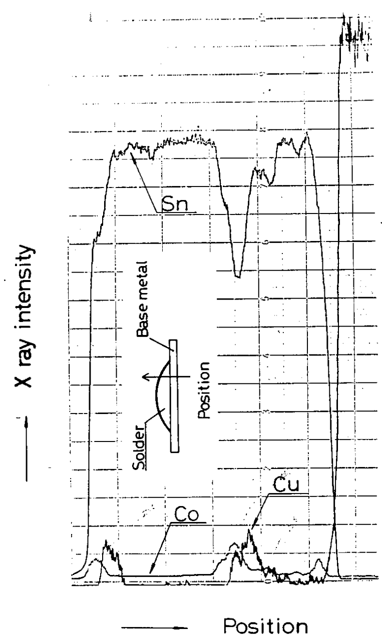

Fig. 10. X-ray micro-analysis of Co, Sn and Cu of cross section of Sn solder spread on coppertplate with $CoSO_4 \cdot 7H_2O$.

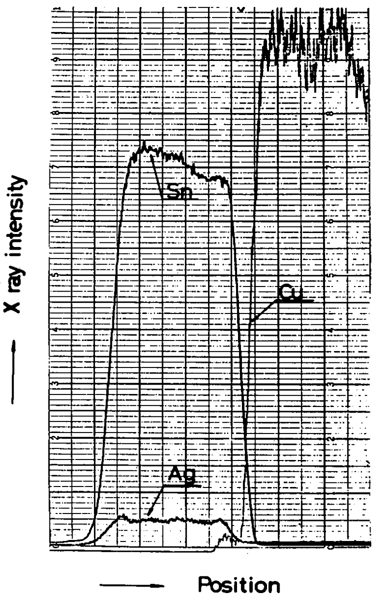

Fig. 11. X-ray micro-analysis of Ag, Sn and Cu of cross section of Sn solder spread on copper plate with Ag_2SO_4.

→ noble
Sn, Co, Cu, Pb, Pd, Bi, Ni, Ag

It may be considered that Na, K, Zn, Al and Mg, of which sulfate have scarcely the effect on spreading, and which dissolve little into Sn from the flux are more base than Sn. In this section, electrochemical series of sulfate in molten salt was compared with the electrochemical series of NaCl-$AlCl_3$ as the electrochemical series in molten metal sulfate isn't given, and the two electrochemical series showed a strong similarity. But, it is recognized that Ag is the most noble from the result of sulfate. From above mentioned results, it is cleared that reactivility with molten Sn as shown in follow eq-(6) is very important factor on spreading with metal sulfate.

$$MSO_4 + Sn \xrightarrow{\triangle} SnSO_4 + M-(Sn) \qquad (6)$$

3.3 The effect of various metal nitrates on spreading

The corrosion (oxidation) behavior of Cu in molten $NaNO_3$ or KNO_3 have been widely studied[10], and it is expected that nitrate shows different action of spreading by oxidation of Cu base metal against sulfate or chloride. The effect of various metal nitrates on spreading was investigated as well as in section 3.1 and 3.2. The results of these spreading tests are shown in **Fig. 12** and **Fig. 13.**

As shown in figures, addition of nitrate of metals which are comparatively base on electrochemical series in aq. solution as like with chlorides and sulfate shows scarcely the effect on spreading, and nitrate of

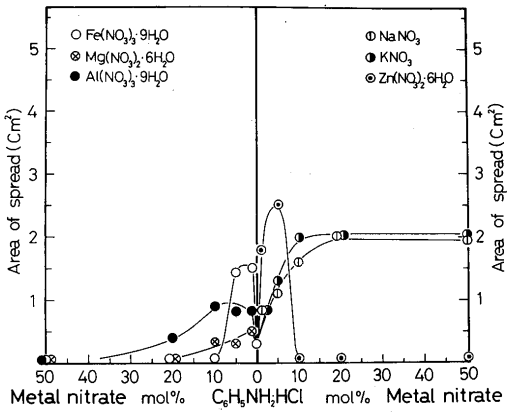

Fig. 12. Spreading of Sn solder on copper plate with $C_6H_5NH_2 \cdot HCl$ $/M(NO_3)_n$ flux at 250 °C.

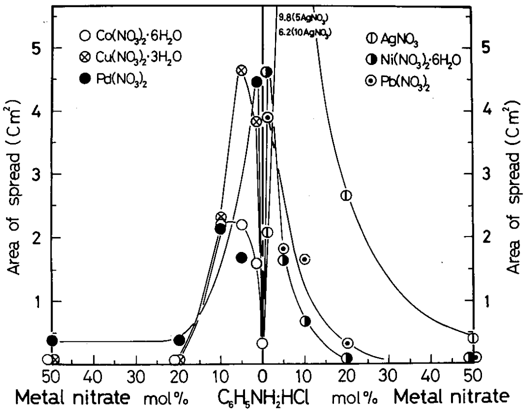

Fig. 13. Spreading of Sn solder on copper plate with $C_6H_5NH_2 \cdot HCl$ $/M(NO_3)_n$ flux at 250℃.

metal (Ag, Ni, Pb, Cu, Co and Pd) which is noble is effective to spread. And then, spread area increases largely by addition of small quantity.

Owing to clear the reaction between molten Sn and nitrate, EMX analysis was adopted, and parts of these results are shown in **Fig. 14, 15** and **16.** In the case of nitrate, the dissolution of Ag, Ni, Pb, Cu, Co and Pd into Sn solder was acknowledged as well as in sulfate and chloride. And it was cleared that dissolution of Zn, Al and Mg into Sn solder was not acknowledged, and reaction did not proceed. Nevertheless, the addition effect on spreading is acknowledged unlike with sulfate and chloride in the case of nitrate of metal such as Na, K, Zn and Fe. And this cause is pursued in next pargraph. Electrochemical series is set up on the basis of the results of maximum values of spread area and the results of EMX analysis, in the case of nitrate as follows;

→ noble
Sn, Co, Pb, Pd, Ni, Cu, Ag

And it may be considered that Zn, Al and Mg of

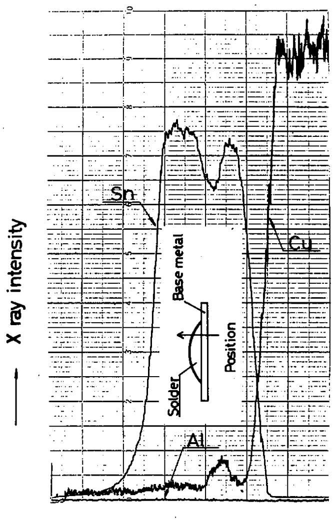

Fig. 14. X-ray micro-analysis of Al, Sn and Cu of cross section of Sn solder spread on copper plate with $Al(NO_3)_3 \cdot 9H_2O$

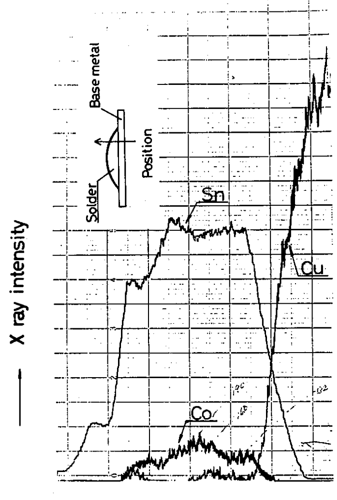

Fig. 15. X-ray micro-analysis of Co, Sn and Cu of cross section of Sn solder spread on copper plate with $Co(NO_3)_2 \cdot 6H_2O$.

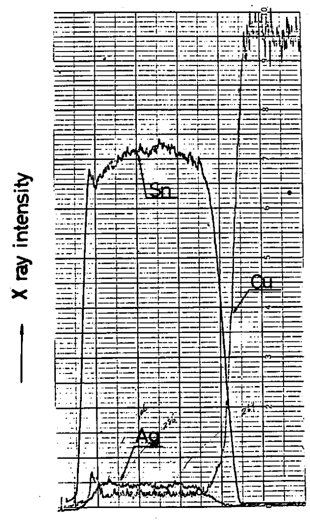

Fig. 16. X-ray micro-analysis of Ag, Sn and Cu of cross section of Sn solder spread on copper plate with $AgNo_3$.

which dissolution into Sn isn't acknowledged is more base than Sn. The electrochemical series of metals is different in solvent, and electrochemical series at 340°C in $NaNO_3$ is given as follows[9];

→ noble

Na, Mg, Pb, Ni, Co, Cu, Ag

In the two electrochemical series, it was shown that Cu and Ag are most noble, and both show very similar order. From above results, it is cleared that important factor controlling spread in the case of metal nitrate depends on electrochemical series (reactivity).

3.4 The effect of sulfates and nitrates of Na, K, Zn and Fe on spreading

In comparison with Fig. 7 and Fig. 12, the difference of the effect on spread in metal sulphate and and nitrate flux (Na, K, Zn and Fe) is remarkable. Owing to clear the cause, the results of EMX analysis are shown in **Fig. 17, 18, 19** and **20** in the case of Na salts and Zn salts respectively.

From the results of EMX analysis, the dissolution of Cu into Sn solder is scarcely acknowledged in the case of sulfate·flux. However, the dissolution of great amount of Cu into Sn solder is acknowledged in the nitrate. The difference to spread between sulphate and nitrate from the results of EMX analysis may be considered as follows; Only Cu salt produced by the reaction of the flux with the base metal in the case of nitrate is effective to spread, because Zn and Na salts do not react with solder. Namely, it is reported[10] that the corrosion reaction between molten $NaNO_3$ and Cu is proceeded. CuO is formed on the

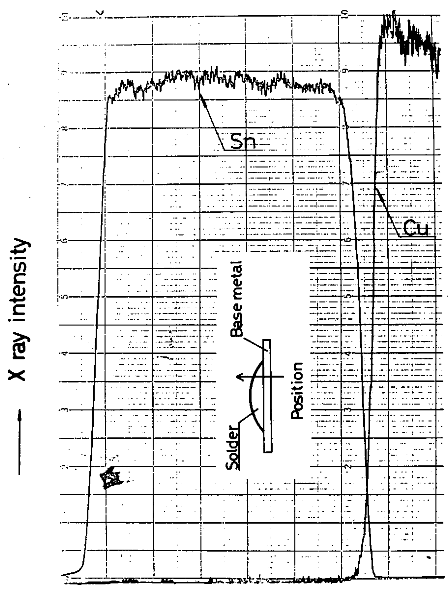

Fig. 17. X-ray micro-analysis of Sn and Cu of cross section of Sn solder spread on copper plate with Na_2SO_4.

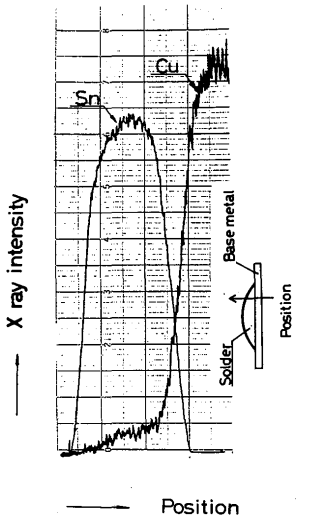

Fig. 18. X-ray micro-analysis of Sn and Cu of cross section of Sn solder spread on copper plate with $NaNO_3$.

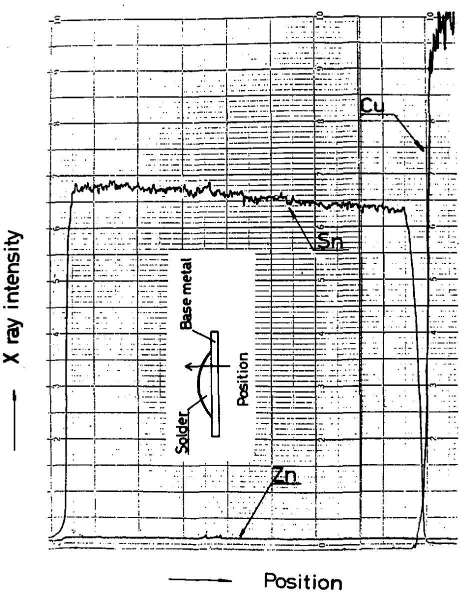

Fig. 19. X-ray micro-analysis of Zn, Sn and Cu of cross section of Sn solder spread on copper plate with Zn $SO_4 \cdot 7H_2O$.

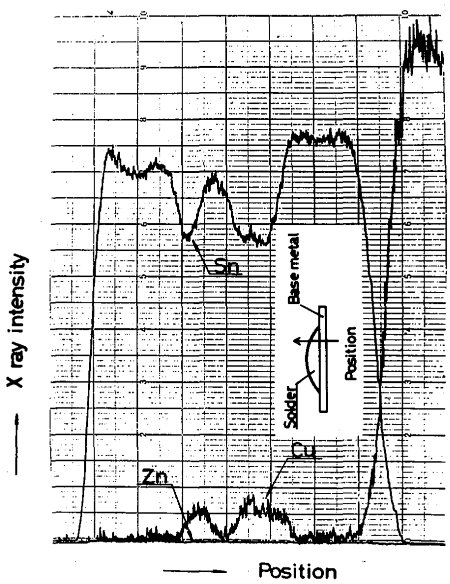

Fig. 20. X-ray micro-analysis of Zn, Sn and Cu of cross section of Sn solder spread on copper pl te with $Zn(NO_3)_2 \cdot 6H_2O$.

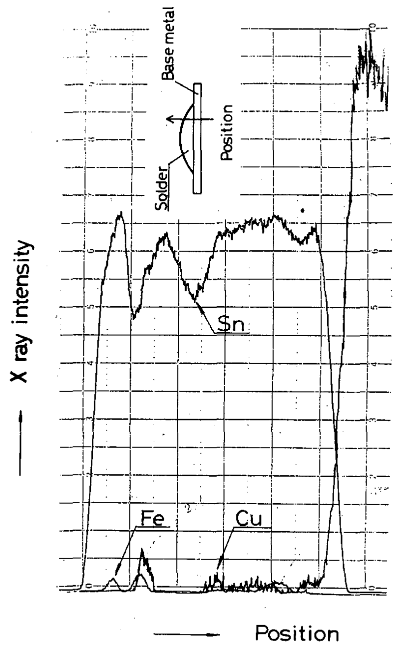

Fig. 21. X-ray micro-analysis of Fe, Sn and Cu of cross section of Sn solder spread on copper plate with $Fe(NO_3)_3 \cdot 9H_2O$.

surface of base metal (Cu) and immediately, Cu salts which produced by the reaction of CuO with $C_6H_5NH_2 \cdot HCl$ react with molten Sn and Cu metal dissolves into Sn solder. And then, it is considered that spread area is improved by the reaction and the dissolution as shown in earlier paper[7, 8]. As shown in **Fig. 21,** in the case of Fe-nitrate, the dissolution of Fe and Cu in Sn solder is acknowledged, and it may be considered that spread area is increased by the reaction of Fe-nitrate and Sn solder, because metallic Fe becomes more nobler than Sn in molten nitrate.

4. Conclusion

By investigating the reaction between molten Sn and inorganic metal salts or the spreading phenomenon of Sn solder on Cu, the flux action of various inorganic metal salts was clarified as follow;

Various metal chlorides, sulfates and nitrates react with molten Sn solder, and this reaction is controlled by electrochemical series of metal in molten salt.

The effect of metal salt on spreading are closely dependent on the reaction between metal salt and molten Sn or the dissolution of metal into Sn solder from the salts.

The difference of the flux action among chlorides, sulfates, and nitrates was slight, and the salts are nearly similar in their effect on the reaction.

Acknowledgement

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