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Studies on Flux Action of Soldering (Report VIII)[†]

—Dissolution and Adsorption Effect—

Ikuo OKAMOTO* and Akira OMORI**

Abstract

The effect of various dissolution processes of metal in solder on wetting was studied. Reaction of metallic salt or of metal from metal salt with solder showed a great effect on wetting. The improvement of wetting may be considered to be due to lowering of interfacial energy by the formation of intermetallic compound at the edge of drop. Moreover, the effect of adsorption of metal ion on Hg surface on wetting was studied.

1. Introduction

In the course of our investigations^(1,2,3), on flux action of soldering, it has been made clear that molten solder reacts with metallic salt in flux, and a metal produced by the reaction dissolves immediately in solder. The above reaction and dissolution are important factors controlling wet of solder on copper plate. When the reaction takes place on solder, streaming of solder is observed and wetting increases.

In this report, we show the relation between the process of dissolution of metal in solder and wetting. And the factor controlling wet was discussed. Moreover, the effect of metallic salt on wetting of mercury in aqueous solution, of which interfacial tension with metallic salt has studied sufficiently by many researchers, is studied on copper plate.

2. Experimental Procedure

The same apparatus and test specimens for spreading test of previous studies^(1,2) were used. Commercially available reagent-grade stearic acid, metal sulfates and nitrates were used as flux after drying. The distribution of elements dissolved in solder was examined by EPMA.

3. Result and Discussion

3.1 Effect of dissolving Cu in solder on wetting

As described in previous paper⁽²⁾, the metal dissolution of flux in solder was detected by EPMA, when metallic salt flux accelerated wetting of solder on copper plate.

In this section, the effect of various dissolution processes of metal in solder on wetting was studied as

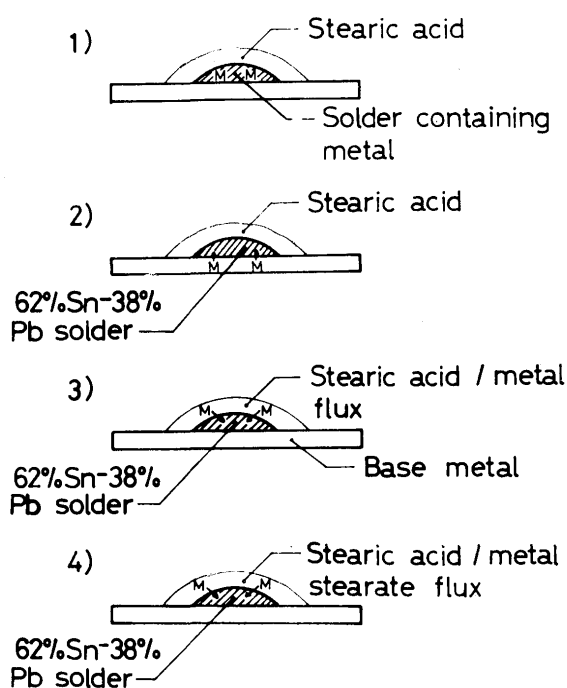


Fig. 1. Dissolution of metal into solder.

shown in **Fig. 1.**

The four methods of dissolving copper are shown as follows:

- 1) 1 wt% copper added previously in Sn-Pb eutectic alloy
- 2) Dissolution of copper from copper substrate
- 3) Dissolution of copper from stearic acid/1 wt% metallic copper powder system flux
- 4) Dissolution of copper from copper stearate flux

By means of above methods for dissolution, the wetting was experimented on copper plate for 10 mins at 240°C, using 0.1 g flux and Sn-Pb eutectic alloy. In the case of (2), spreading test was tried with heating

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- 1) Addition of 1%Cu to Sn-Pb eutectic solder
- 2) Dissolution of base metal in solder
- 3) Metal copper/stearic acid flux
- 4) Dissolution of copper produced by the reaction of metal stearate with solder

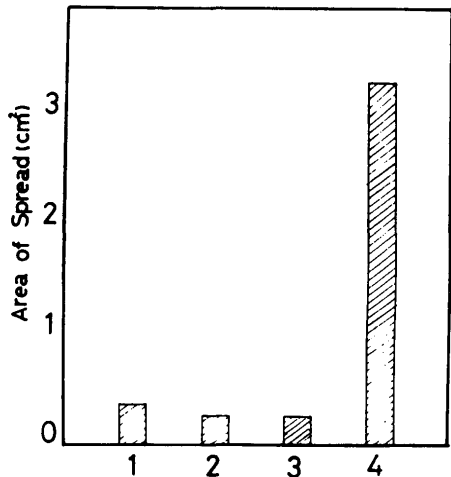


Fig. 2. Spreading in the case of various dissolutions of Cu into solder in Fig. 1.

for longer than 10 mins to know the effect of dissolution on wetting with time. The results obtained are shown in Fig. 2. From the figure, the dissolution of copper in the case of (2) and (3) or the existence of copper in solder was not effective for wetting under the conditions. However, only in the case of (4), the effect of dissolution of copper on wetting was recognized markedly. A great amount of copper in solder is analyzed by EPMA. (see Fig. 4).

From the above results, active atomic copper, which produced by the reaction of Sn in alloy with copper stearate, showed a great effect on wetting. The effect of the copper on wetting may be explained as follows: The active copper reacts immediately with molten Sn at the surface of molten Sn-Pb alloy solder, then Sn-Cu intermetallic compound is formed easily. The interfacial energy becomes consequently low⁴⁾. Thus, the wetting of solder on copper plate is promoted. Distribution of copper in Sn-Pb alloy is shown in Fig. 3 and Fig. 4, respectively in the case of (3) and (4). On the other hand, the energy change at the edge of the drop does not take place markedly, so wetting did not improve.

3.2 Effect of dissolving Ni in solder on wetting

The effect of dissolution of Ni on wetting was examined on Ni plate by the four similar methods as in the case of copper dissolution.

The results are shown in Fig. 5. In order to know the dissolving of Ni in solder, the cross section

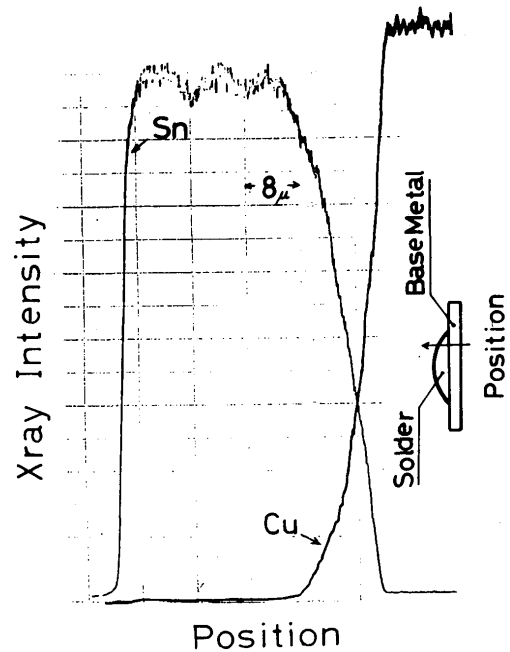


Fig. 3. Chart of X-ray micro-analysis of Sn and Cu for the cross section of test specimen in the case of (3) in Fig. 1.

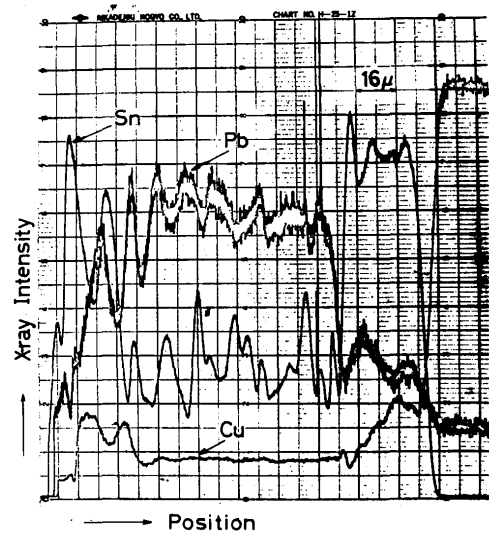


Fig. 4. Chart of X-ray micro-analysis of Sn, Pb and Cu for the cross section of test specimen in the case of (4) in Fig. 1.

- 1) Addition of 1% Ni to Sn-Pb eutectic solder
- 2) Dissolution of base metal in solder
- 3) Metal nickel / stearic acid flux
- 4) Dissolution of nickel produced by the reaction of metal stearate with solder

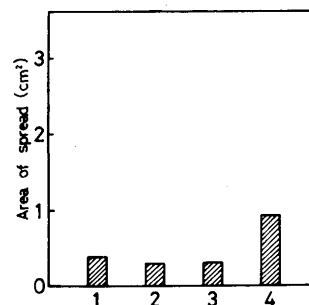
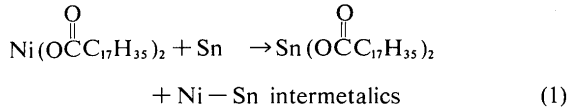


Fig. 5. Spreading in the case of various dissolutions of Ni into solder in Fig. 1.

of specimens after wetting was analyzed by EPMA. Line analyses were shown in Fig. 6 for the case of (3) and in Fig. 7 for the case of (4). From these figures, spreadability for solder on Ni plate was improvement only by dissolving of Ni by the reaction of nickel stearate with Sn. (eq.-(1))



The formation of Ni-Sn intermetallic compound

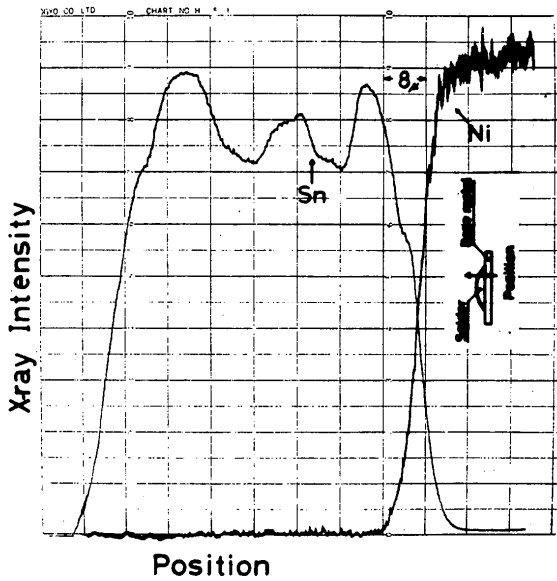


Fig. 6. Chart of X-ray micro-analysis of Sn and Ni for the cross section of test specimen in the case of (3) in Fig. 1.

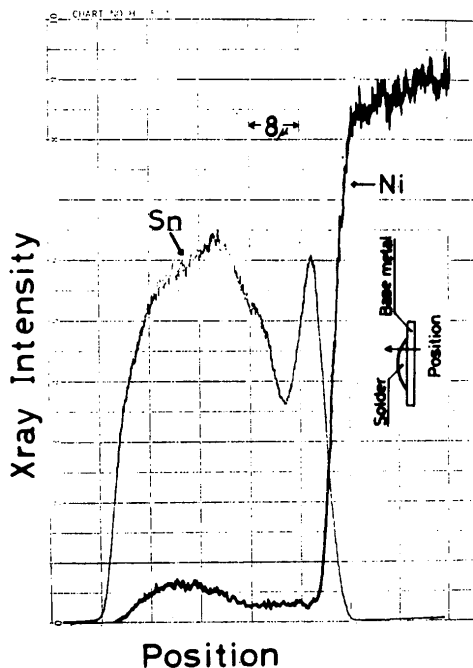


Fig. 7. Chart of X-ray micro-analysis of Sn and Ni for the cross section of test specimen in the case of (4) in Fig. 1.

results in good wetting of solder, because active atomic nickel reacts easily with Sn. However, Ni-stearate showed smaller effect on wetting than Cu stearate. It may be dependent on the difference of reactivity with molten Sn-Pb alloy as described in the earlier paper.

In this experiment, one can not discriminate between dissolving of metal from metallic stearate and dissolving from base metal, with regard to dissolution of metal in solder. So, in order to clarify the difference, spreading was tried in copper stearate/nickel substrate system. The result of EPM analysis of the test specimen shows the dissolution of copper from copper stearate. From above dissolution test results, we note that the dissolution of metal from copper stearate flux on nickel plate shows a great effect on wetting also. It has been elucidated^{11,2)} that metal stearate of Ag, Pb and Ni or metallic chloride of Ag, Co, Cu, Ni etc. showed a good effect on improvement of wetting and the dissolution of each metal from above salts was recognized. So, it is considered that such improvement of wetting is dependent on the lowering of interfacial energy by the formation of intermetallic compound between Sn and active metal, which given by the reaction of metallic salt with Sn at the surface of solder.

3.3 Effect of various metallic salts on wetting of Hg on copper plate

By investigating the dissolution of metal in solder, it was recognized that the phenomenon on interface between flux and solder resulted in an important factor

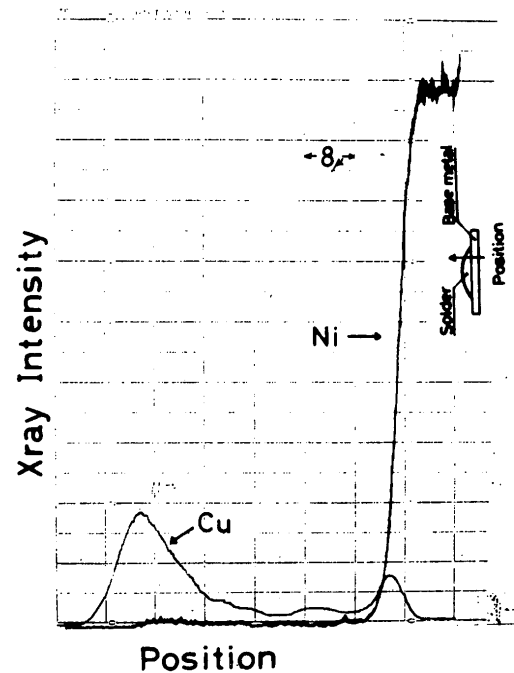


Fig. 8. Chart of X-ray micro-analysis of Ni and Cu for the cross section of test specimen spread of Sn-Pb eutectic alloy on nickel plate with Cu-stearate.

controlling wet of solder. The cause for improving wet was considered to be lowering of interfacial energy by the occurrence of intermetallic compound on the interface. In order to elucidate wetting, the effect of various metal salts on wetting of Hg was studied on copper plate in aqueous solution, in comparison with past studies on interfacial tension of Hg in aqueous solution.

3.3.1 Effect of interfacial tension

As is well known, polarographic maximum is provoked by the spontaneous streaming of Hg and electrolysis solution along the interface. This is due to the difference of interfacial tensions at the upper and lower end of the Hg drop. A streaming at a stationary Hg surface were observed experimentally⁵⁾, namely:

1) by the addition of an oxidizing or reducing agent, by which the potential of Hg is changed according to the Nernst formula resulting in the local difference of interfacial tension. This is expected from the electro-capillary curve, shown in Fig. 9.

2) by the addition of a surface-active substance, by which the interfacial tension is locally.

In order to know the effect of above streaming on wetting of Hg on copper plate, the change of spread was studied in water by the addition of anionic surface active reagent KI, as shown in Fig. 10. By adding KI, a streaming at Hg surface takes place, thus wetting increases. This phenomenon is due to the change of

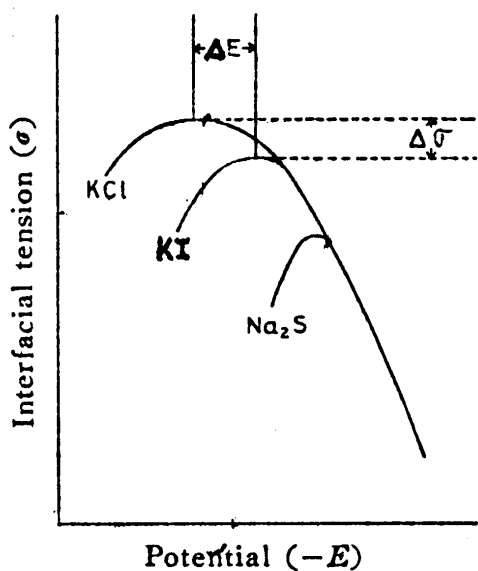


Fig. 9. Typical electro-capillary curve.

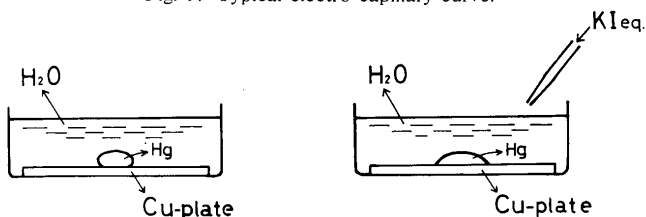


Fig. 10. Effect of addition of KI on wetting.

Table 1. Effect of addition of metal chloride to water on wetting of Hg.

Metal chloride	Concentration of metal chloride flux		
	Saturated aq.	0.5 mol aq.	0.1 mol aq.
	Spreading after 1 sec.	Spreading after 1 sec.	Spreading after 1 sec.
FeCl ₃	⊙	⊙	⊙
CuCl ₂	⊙	○	○
AlCl ₃	⊙	○	○
PdCl ₂	⊙	○	○
BiCl ₃	⊙	○	○
KCl	X	X	X
CaCl ₂	X	X	X
NaCl	X	X	X
MgCl ₂	X	X	X
CsCl	X	X	X



Table 2. Effect of addition of metal nitrate to water on wetting of Hg.

Metal nitrate	Concentration of metal nitrate flux		
	Saturated aq.	0.5 mol aq.	0.1 mol aq.
	Spreading after 1 sec.	Spreading after 1 sec.	Spreading after 1 sec.
Fe(NO ₃) ₃	⊙	⊙	⊙
Cu(NO ₃) ₂	○	○	X
AgNO ₃	⊙	○	○
Al(NO ₃) ₃	○	○	X
Bi(NO ₃) ₃	○	○	○
KNO ₃	X	X	X
Ca(NO ₃) ₂	X	X	X
NaNO ₃	X	X	X
Mg(NO ₃) ₂	X	X	X



interfacial tension, namely a lowering of interfacial tension by adding KI in water. Moreover, the effect of various metallic salts on wetting was studied by the same method as in the case of KI. The results obtained were shown in Table 1 and Table 2.

Two types of metal ion effect of salts are summarized as follows:

- 1) Fe⁺⁺⁺, Al⁺⁺⁺, Bi⁺⁺⁺, Cu⁺⁺, Ag⁺⁺ and Pd⁺⁺ which show a great effect on wetting
- 2) K⁺, Na⁺, Ca⁺⁺ and Mg⁺⁺, which show little effect on wetting

About adsorption of ion on Hg surface, Nagaura⁶⁾ states that degree of adsorption of ion on Hg surface may be dependent on the difference potential between point of zero change of Hg (p. z. c) and normal potential of ion. The relation between p. z. c of Hg and normal potential of metal ion is shown in Fig. 11.

From the figure, metal ions such as Na⁺, K⁺, Ca⁺⁺

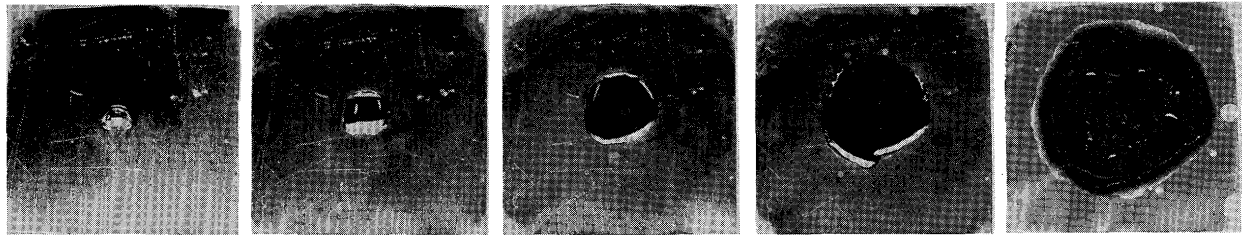


Photo. 1. Degree of wetting of Hg on Cu plate in aqueous $\text{Fe}(\text{NO}_3)_3$ solution with time.

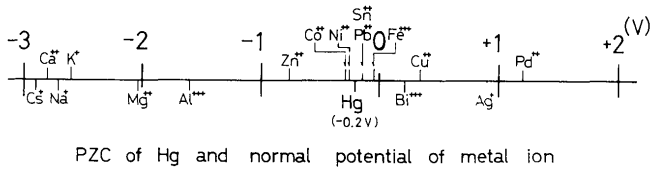


Fig. 11. Relation between p. z. c of Hg and normal potentials of metal.

and Mg^{++} , have high normal potential and are adsorbed weakly on Hg surface. However, about metal ion such as Al^{+++} , Bi^{+++} and Fe^{+++} we may not be understood clearly to have such great effect on wetting from Fig. 11. Because these metal ions have large charge, these ions may be adsorbed strongly on Hg surface. And, spreading is promoted. As Ag and Pd are more noble than Hg, the reaction between Hg and these ions takes place on Hg surface, thus spreading increases. In the case of $\text{Fe}(\text{NO}_3)_3$, degree of wetting of Hg on copper plate is shown with time in **Photo. 1**.

From the above results, the lowering of interfacial tension causes spread to increase, by the adsorption of metal ion on Hg surface or reaction between Hg and metal ion.

3.4 Factor controlling wet

In above sections, the effect of reaction or adsorption at solder surface was studied regarding wetting. Factors controlling wet were taken into consideration in this section on the basis of such results.

If liquid in the form of a drop is placed on the surface of a solid, it is found to make contact and spread. Depending on the relative values of the surface tensions acting at the edge of the drop, the area of contact between the drop and the substrate increases. Generally, there are two types in spreading, namely, self spreading and forced spreading. In self spreading, spreading is determined by the magnitudes of surface and interfacial forces. However, on forced spreading, where a stress is applied to a system which is initially at equilibrium, one of the interfaces may be propelled relative to the others. Many examples of both self and forced spreadings occur in practice.

When above metallic salts are used as flux, practical systems where spreading is occurring are never at equilibrium.

In spreading using flux, such as copper stearate etc. the reaction of molten alloy with metallic salt takes place on the interface and metal produced by the reaction attaches a metal in solder to form intermetallic compound. The formation of intermetallic compound causes the interfacial energy to lower at the edge of the drop. (see **Fig. 12**) Depending on the relative reactivity between solder and metallic salt acting at the edge of the drop, spreading increases. The relation between the reactivity and spreading was described in previous paper³⁾, we note that the more the reaction of flux with solder precedes, the larger the spread becomes.

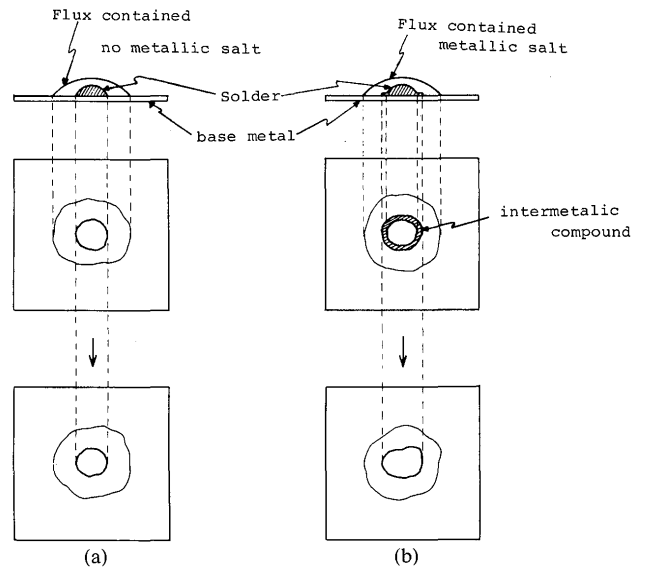


Fig. 12. Schematic diagram for spreading, when intermetallic compound forms or not. (a) no change of wetting (b) improvement of wetting

Fig. 12 shows schematic diagram for spreading, when intermetallic compound forms (a) or not (b). However, if intermetallic compound forms on the solder surface, m. p. of the compound is much higher than temperature for soldering and does not dissolve easily into solder, we note that the spreading obstructs⁷⁾.

4. Conclusion

The effect of reaction and adsorption on wetting

was studied. Reaction of metallic salt or of metal from metal salt with solder shows a great effect on wetting. Depending on the lowering of interfacial tension by the formation of intermetallic compound at the edge of drop, spread increases.

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