| Title | Electrochemical Actions of Flux for Soldering |
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| Author(s) | Okamoto, Ikuo; Onishi, Iwao |
| Citation | Transactions of JWRI. 1975, 4(1), p. 71-78 |
| Version Type | VoR |
| URL | https://doi.org/10.18910/8413 |
| rights | |
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# Electrochemical Actions of Flux for Soldering[†]

Ikuo OKAMOTO* and Iwao ONISHI**

## Abstract

In order to confirm the electrochemical actions of flux, which contained $H^+$ and $Cl^-$ ions, for soldering, the spreading test of a low melting point solder on copper base metal and the corrosion potential measurements of the base metal and solder in the studied flux solution were made.

Through the experiments and considerations, a new experimental equation, $\log a_{Cl^-} = -4.65 + pH$, which defines whether the solder does spread or doesn't, was introduced.

## 1. Introduction

The actions of flux for soldering and brazing, in general, have been considered to date as follows;

1) To dissolve or releasen any oxides present on the base metal and molten filler alloy surfaces which are to be joined.
2) To prevent the oxidation of these surfaces during the joining process.
3) To lower the surface tension of the molten filler alloy, namely, the molten flux should be readily displaced by the molten filler alloy, thus promoting the wetting of the base metal · by the molten filler alloy.

In these factors, the reports on the dissolution mechanic of the base metal and molten filler alloy oxides are very few in the past literature. The report of M. F. Jordan[1] et al. is one of them. They reported about the electrochemical action of flux for brazing of aluminum and considered about the anodic corrosion reaction of a local cell, which forms between aluminum base metal and aluminum oxide film on the base metal in molten flux used. This theory is apparently a good idea for aluminum, but will not be applied for copper because copper presents in noble side than hydrogen in the ionic series.

The purpose of this paper was to investigate the electrochemical action of flux for soldering of copper. In order to easy the consideration for the results obtained, aqueous solutions of $H_2SO_4$, $H_2SO_4 + NaCl$ and HCl were selected as the fluxes, and a low melting point alloy of 47°C was used as the solder. Two experiments were made; ordinary spreading tests and corrosion potential measurements of the base metal and solder in flux solutions used. Both relation was considered under a thermo-dynamical equilibrium condition to clarify the electrochemical actions of $H^+$ and $Cl^-$ ions present in the flux solutions. This consideration made it possible to introduce a new experimental equation, which denotes a critical condition of the flux concentration that defines whether the used solder does spread or dosen't on the base metal.

## 2. Materials, Apparatus and Procedure Used

### 2.1 Spreading test

The base metal used is pure copper plate, the size of $40 \times 40 \times 0.5$ mm thick. Each surface of the specimen was degreased, electrolytic polished, water washed and dried. The solder used is a low melting point alloy as shown in **Table 1**. This solder was selected to protect the constituent variation of the used flux solution through the spreading test, its test temperature was 60°C and spreading time 60 sec. **Figure 1** shows the experimental apparatus for spreading test. The test was made on the base metal placed

Table 1. Chemical compositions of solder used.

| Composition (wt.%) | | | | | Melting point (°C) |
|---|---|---|---|---|---|
| Cd | Sn | In | Bi | Pb | |
| 5.3 | 8.3 | 19.1 | 44.7 | 22.6 | 47 |



M - Mantle Heater
V - Voltage Regulator
C - Temperature Controller
T - Test Piece
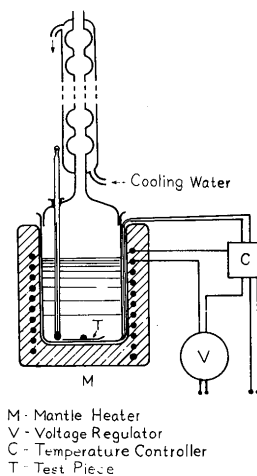
Fig. 1. Schematic diagram of solder-spread test apparatus.

horizontally in the glass bottom filled with the flux solution. The buttom of solder, 0.3gr, was placed on the center of the base metal. Through the test, the solution concentration is holded constantly because the vapor generated under the test temperature is condenced by a cooling water tube attached to the bottle. After the spreading was finished, the specimen is removed from the bottle and the spreading area was measured with a planimeter.

Three flux solutions were used; The first is an aqueous solution of $H_2SO_4$ as flux solution containing $H^+$ ion only, namely no $Cl^-$ ion. The second is the mixed flux solution which prepared to know the effect of $Cl^-$ ion. This solution contains the required amount of NaCl within aqueous solution of $H_2SO_4$ of each pH, as shown in **Table 2**. The $H^+$ and $SO_4^{--}$ ion concentrations showed in the table are chemical analysis values. The difference of pH value and this concentration value means the dissociation of water produced essentially by a neutralization method of chemical analysis. NaCl values show the addition content. $\Gamma$ and $\mu$ values indicate total ion concentration and ionic strength of each solution and also $a_{Cl^-}$, that is activity of $Cl^-$ ion, was calculated from $f_{Cl^-}$ that is activity coefficient of $Cl^-$ ion, which was obtained from Kielland Table[2]. The third flux solution is an aqueous solution of HCl. An $a_{Cl^-}$ of that solution

of each pH was calculated with the same method under full dissociation condition, to compare with those of the mixed flux solution.

## 2.2 Corrosion potential measurement

**Figure 2** is a schematic diagram for measuring of corrosion potential. A reference electrode is a saturated calomel electrode and a reserver filled saturated KCl aqueous solution is inserted to between the reference electrode and a cell contained the test piece, which is either base metal or solder, preventing the dilution of the $Cl^-$ ion concentration in the reference electrode.
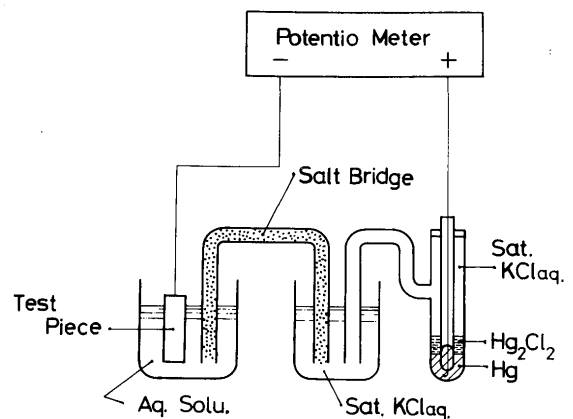


Fig. 2. Circuit diagram for measuring corrosion potential.

Table 2. Calculated $a_{Cl^-}$ values of mixed flux aq. solutions.

| pH | H+ g-ion/l | SO₄⁻ g-ion/l | NaCl mol/l | $\mu \times 10^2$ | $\Gamma \times 10^2$ | $f_{Cl^-}$ | $a_{Cl^-} \times 10^3$ | $a_{Cl^-}$ of HCl $\times 10^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | $8.20 \times 10^{-1}$ | $4.10 \times 10^{-1}$ | $1 \times 10^{-3}$ | 123 | 246 | 0.555 | 0.565 | 35.7 |
| | | | $1 \times 10^{-2}$ | 124 | 248 | 0.564 | 15.64 | |
| | | | $3 \times 10^{-2}$ | 126 | 252 | 0.563 | 16.9 | |
| | | | $5 \times 10^{-2}$ | 128 | 256 | 0.562 | 28.1 | |
| | | | $7 \times 10^{-2}$ | 130 | 260 | 0.560 | 39.2 | |
| | | | $9 \times 10^{-2}$ | 132 | 264 | 0.558 | 50.2 | |
| | | | $1 \times 10^{-1}$ | 133 | 266 | 0.557 | 55.7 | |
| 2 | $14.4 \times 10^{-3}$ | $7.20 \times 10^{-3}$ | $1 \times 10^{-3}$ | 2.48 | 4.48 | 0.855 | 0.855 | 7.00 |
| | | | $5 \times 10^{-3}$ | 2.64 | 5.28 | 0.845 | 4.23 | |
| | | | $1 \times 10^{-2}$ | 3.14 | 6.28 | 0.833 | 8.73 | |
| | | | $3 \times 10^{-2}$ | 5.15 | 10.3 | 0.796 | 23.9 | |
| | | | $5 \times 10^{-2}$ | 7.15 | 14.3 | 0.774 | 38.7 | |
| | | | $1 \times 10^{-1}$ | 14.15 | 24.3 | 0.734 | 73.4 | |
| 2.5 | $2.80 \times 10^{-3}$ | $1.40 \times 10^{-3}$ | $1 \times 10^{-3}$ | 0.52 | 1.04 | 0.922 | 0.922 | 4.08 |
| | | | $2 \times 10^{-3}$ | 0.62 | 1.24 | 0.915 | 1.83 | (4.40mol/l) |
| | | | $3 \times 10^{-3}$ | 0.72 | 1.44 | 0.910 | 2.73 | |
| | | | $4 \times 10^{-3}$ | 0.82 | 1.64 | 0.905 | 3.62 | |
| | | | $5 \times 10^{-3}$ | 0.92 | 1.84 | 0.900 | 4.50 | |
| | | | $1 \times 10^{-2}$ | 1.42 | 2.84 | 0.860 | 8.60 | |
| | | | $4 \times 10^{-2}$ | 4.42 | 8.84 | 0.807 | 32.3 | |
| | | | $5 \times 10^{-2}$ | 5.40 | 10.8 | 0.794 | 39.7 | |
| | | | $1 \times 10^{-1}$ | 10.40 | 20.80 | 0.746 | 74.6 | |
| 3.0 | $7.8 \times 10^{-4}$ | $3.9 \times 10^{-4}$ | $1 \times 10^{-3}$ | 0.217 | 0.434 | 0.947 | 0.947 | 2.78 |
| | | | $1 \times 10^{-2}$ | 1.11 | 2.23 | 0.891 | 8.91 | |
| | | | $3 \times 10^{-2}$ | 3.11 | 6.23 | 0.832 | 25.0 | |
| | | | $4 \times 10^{-2}$ | 4.16 | 8.23 | 0.813 | 32.5 | |
| | | | $5 \times 10^{-2}$ | 5.10 | 10.2 | 0.797 | 39.9 | |
| | | | $1 \times 10^{-1}$ | 10.10 | 20.2 | 0.799 | 79.9 | |

The whole surface area, but except for the exposure area of $10 \times 10$ mm on one side, of the test piece was insulated with a paint. The exposure part and a tip of the salt bridge were then immersed 5 mm apart in the solution, suspending to 20 mm below the water level. The corrosion potential was measured with a potentiometer.

## 3. Results and Discussions

### 3.1 Effects of the concentrations of $H^+$ and $Cl^-$ ions on the spreading of solder

**Figure 3** shows the relation between the spread area of the solder and pH of the used flux solutions. In this experiment, the $Cl^-$ ion concentration of the mixed solution of each pH was adjusted as agree with that of the aqueous solution of HCl of each pH, namely, although both solutions are identical with regard to the concentrations of $H^+$ and $Cl^-$ ions, but differ in the constituents.

From this result, it is evident that the higher the concentration of $H^+$ ion in the flux solutions, the better the spread area of solder becomes. On the other hand, both spread areas in the aqueous solutions of HCl and the mixed aqueous solutions at various pH values are about equal. This experimental fact means that both $SO_4^{2-}$ and $Na^+$ ions haven't the effective action for the spreading of the solder and the fluxing action of $Cl^-$ ion is effective with a decreasing concentration of $H^+$ ion in these solutions. Accordingly, the fluxing actions of both $H^+$ and $Cl^-$ ions must be make clear. Moreover, the solder didn't spread in the solutions of pHs 4 and 5.

**Figure 4** shows the effects of $Cl^-$ ions concentrations in the mixed solutions on the spreading of solder when the concentration of $H^+$ ion in the solution is kept about constantly. In this case, since
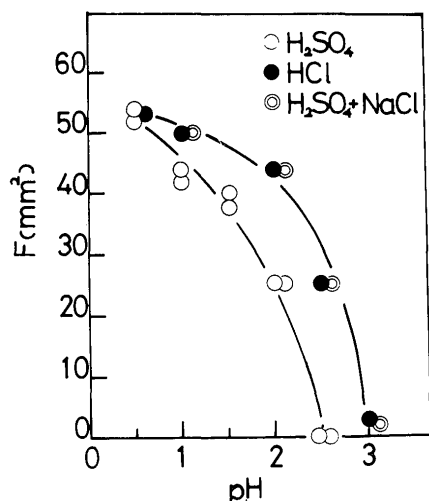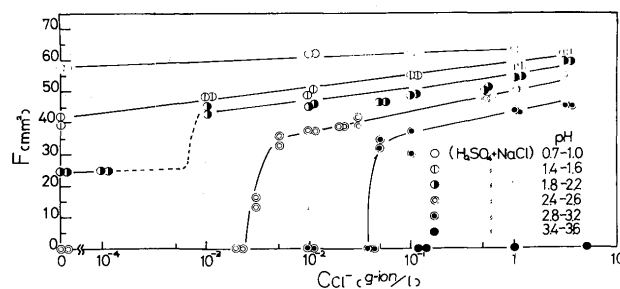


Fig. 4. Relation between spread area of solder and $Cl^-$ ion concentration in mixed flux aq. solution with constant pH.

the excessive addition of NaCl, namely $Cl^-$ ion, into the aqueous solution of $H_2SO_4$ becomes to increase the pH value of its mixed solution, the spreading test was made at a $Cl^-$ ion concentration zero to 5 g-ion/$l$ in the mixed solution, as·shown in the figure. The spread area at each pH, as can be seen in figure, increases slightly with an increasing concentration of $Cl^-$ ion. In addition, the effect of $Cl^-$ ion is remarkable as the pH value of the solution is much, and especially the spread areas of pHs 2.5 and 3.0 increase suddenly at a limitting $Cl^-$ ion concentration, which is $3 \times 10^{-3}$ g-ion/$l$ for pH 2.5 and $5 \times 10^{-2}$ g-ion/$l$ for pH 3.0. This limitting concentration shifts to lower $Cl^-$ ion concentration side as the pH value of the solution decreases. In a domain below this limitting concentration the solder did not spread, while in a domain above this limitting concentration the spread was observed, but the spread area was about a constant as far as the pH of the solution was kept constantly. No papers have been published on this limitting concentration in detail.

From this result, we have considered that a mechanism of fluxing action of $Cl^-$ ion present in the solution may be the limitting concentration of $Cl^-$ ion and the mechanism may be predict by a electrochemical reaction taking place at the base metal /the solution interface. In order to confirm the reaction in the solution, the following electrochemical experiment was made.

### 3.2 Corrosion potential of base metal immersed in flux solution

#### 3.2.1 Changes of potential in an aqueous solution of $H_2SO_4$

The changes of corrosion potentials of copper specimens in the aqueous solutions of $H_2SO_4$ at 25°C as a function of the immersion time are shown in **Fig. 5.** The potentials at pHs 1 and 2 decrease with an increasing of the immersion time, and inversely increase in the case of pHs 4 and 5. In addition the potential at each pH steadies within a few minutes from the initiation of immersion. This steady potential at each pH was replotted in **Fig. 6,** which is the potential-pH



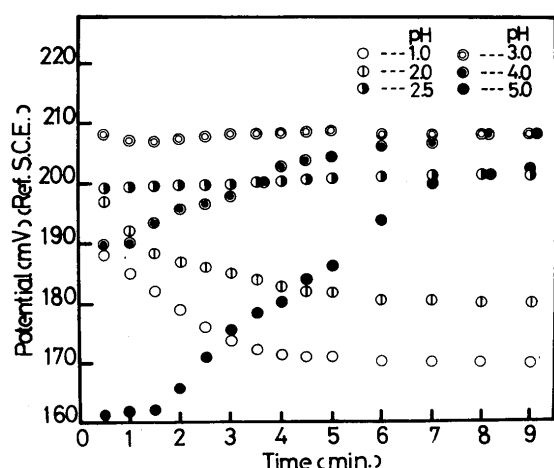Fig. 3. Spread area of solder on copper base plate in various flux aq. solutions at 60°C.

Fig. 5. Variation of corrosion potential on copper in $H_2SO_4$ aq. solution at 25°C.
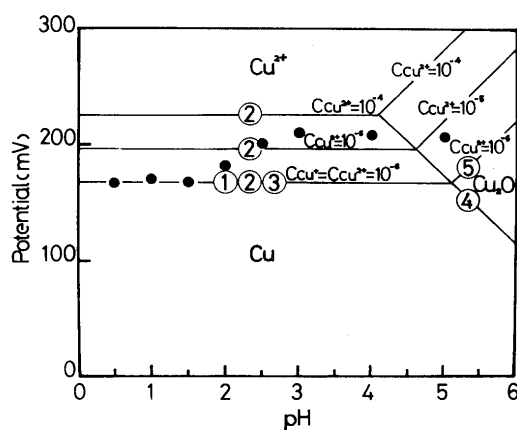


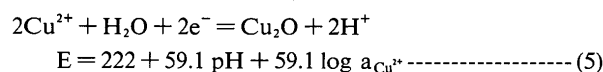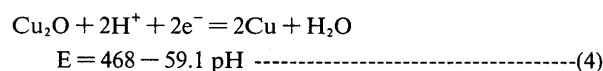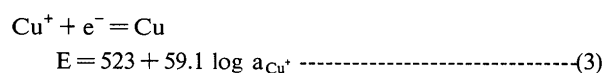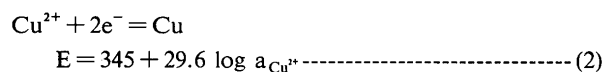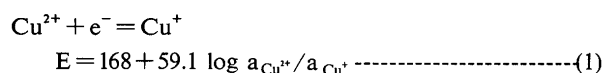Fig. 6. Potential-pH equilibrium diagram for Cu-$H_2O$ system and corrosion potentials indicated in Fig. 5.

diagram for the stable equilibria of the system Cu-$H_2O$ at 25°C. In this system a number of electrode reactions[3] to be considered, in general, are as follows (in mV);

$$Cu^{2+} + e^- = Cu^+$$
$$E = 168 + 59.1 \ \log a_{Cu^{2+}}/a_{Cu^+} \ \text{-----------------------(1)}$$

$$Cu^{2+} + 2e^- = Cu$$
$$E = 345 + 29.6 \ \log a_{Cu^{2+}} \text{----------------------------(2)}$$

$$Cu^+ + e^- = Cu$$
$$E = 523 + 59.1 \ \log a_{Cu^+} \text{-----------------------------(3)}$$

$$Cu_2O + 2H^+ + 2e^- = 2Cu + H_2O$$
$$E = 468 - 59.1 \ pH \ \text{----------------------------------(4)}$$

$$2Cu^{2+} + H_2O + 2e^- = Cu_2O + 2H^+$$
$$E = 222 + 59.1 \ pH + 59.1 \ \log a_{Cu^{2+}} \text{------------------(5)}$$

$$2CuO + 2H^+ + 2e^- = Cu_2O + H_2O$$
$$E = 671 - 59.1 \ pH \ \text{----------------------------------(6)}$$
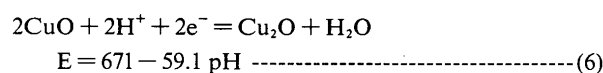
A number on each line corresponds to that of each equation, and these lines were drawed for the potential obtained from the calculation, which was made sub-
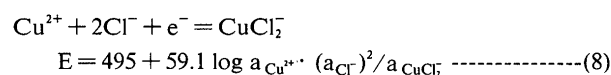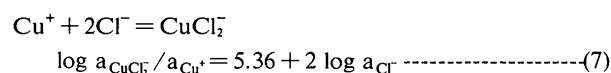
stituting $C_{Cu^{2+}} = 10^{-4}$, $10^{-5}$ and $10^{-6}$, and $C_{Cu^+} = 10^{-6}$ g-ion/$l$ for the activity of logarithm term of the corresponding equation (i. e. : assume that concentration equals activity). These lines form the boundaries of three domains, within which metallic Cu, $Cu_2O$ and $Cu^+$ is absolutely stable,, and the steady potential at pH 5 exists in the domain of the $Cu_2O$, accordingly, it is believed that the reaction of equations (5) proceeds to the right side, so that the resultant product of $Cu_2O$ on the base metal becomes more stable. The steady potentials at pHs 4, 3 and 2 decrease in order of its description, and all exist in the domain of the unstable $Cu_2O$, accordingly, it is belived that the reaction of equation (4) proceeds to the right side, so that the potential migrates with an increasing concentration of $H^+$ ion in the solution to the domain of the more stable metallic Cu, and also coincides with the line, at which the concentrations of $Cu^+$ and $Cu^{2+}$ respectively are $10^{-6}$ g-ion/$l$, whose value is the well known, thermodynamically, limitation concentration that denotes whether corrosion does or doesn't take place.

From above mentioned considerations it may be expected that the spreading of the solder in the aqueous solution of $H_2SO_4$ shown in Fig. 3 depends on the stability of $Cu_2O$ formed on the base metal, of course, since the stability increases as the pH of solution is increased, the spread area decreases. Moreover, the formation of CuO, especially $Cu(OH)_2$, refering to equation (6), would not so much affected against the potential investigated, because the used aqueous solution of $H_2SO_4$ belongs to an acid, medium. We therefore omited it.

### 3.2.2 Effect of $Cl^-$ ion on the corrosion potential of base metal

When the additive contents of $Cl^-$ ions to the aqueous solution of $H_2SO_4$, whose pH is 1, 2 and 3, are $10^{-1}$, $10^{-2}$ and $10^{-3}$ g-ion/$l$, the relation between the corrosion potential of copper specimen and the pH of the mixed solution is shown in **Fig. 7.** As compared with the result of no $Cl^-$ ion, which is Fig. 6, the potential lowers remarkably by the addition of $10^{-1}$ g-ion/$l$ $Cl^-$ ion, although the potentials in the extents of $10^{-2}$ or $10^{-3}$ g-ion/$l$ are similar.

In the ternary system Cu-Cl-$H_2O$, a number of electrode reactions[3] to be considered, in general, are as follows, together with the former equations (in mV):

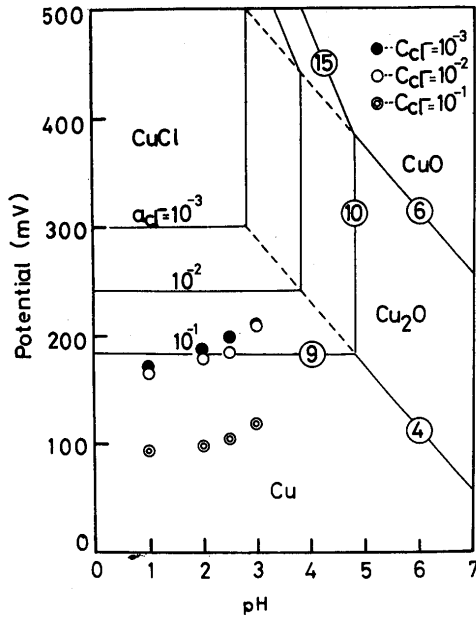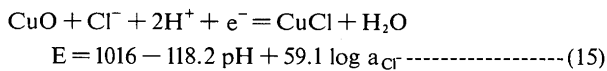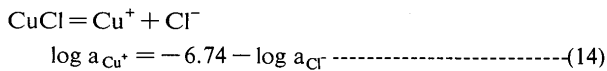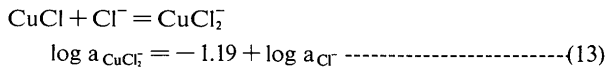$$Cu^+ + 2Cl^- = CuCl_2^-$$
$$\log a_{CuCl_2^-}/a_{Cu^+} = 5.36 + 2 \ \log a_{Cl^-} \text{--------------------(7)}$$

$$Cu^{2+} + 2Cl^- + e^- = CuCl_2^-$$
$$E = 495 + 59.1 \ \log a_{Cu^{2+}} \cdot (a_{Cl^-})^2/a_{CuCl_2^-} \text{--------------(8)}$$
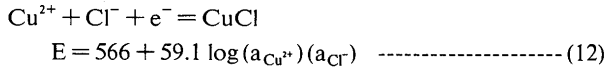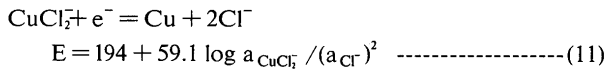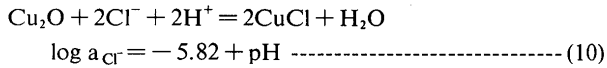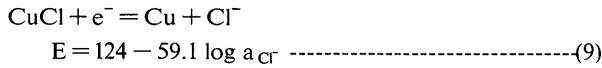
Fig. 7. Potential-pH equilibrium diagram for Cu-Cl-H₂O system and corrosion potentials of copper immersed in mixed flux aq. solutions.

$CuCl + e^- = Cu + Cl^-$

$E = 124 - 59.1 \log a_{Cl^-}$ ----------------------------------(9)

$Cu_2O + 2Cl^- + 2H^+ = 2CuCl + H_2O$

$\log a_{Cl^-} = -5.82 + pH$ -----------------------------(10)

$CuCl_2^- + e^- = Cu + 2Cl^-$

$E = 194 + 59.1 \log a_{CuCl_2^-}/(a_{Cl^-})^2$ -------------------(11)

$Cu^{2+} + Cl^- + e^- = CuCl$

$E = 566 + 59.1 \log (a_{Cu^{2+}})(a_{Cl^-})$ ---------------------(12)

$CuCl + Cl^- = CuCl_2^-$

$\log a_{CuCl_2^-} = -1.19 + \log a_{Cl^-}$ -----------------------(13)

$CuCl = Cu^+ + Cl^-$

$\log a_{Cu^+} = -6.74 - \log a_{Cl^-}$ --------------------------(14)

$CuO + Cl^- + 2H^+ + e^- = CuCl + H_2O$

$E = 1016 - 118.2\,pH + 59.1 \log a_{Cl^-}$ ------------------(15)

In Fig. 7, the full lines based on equations (4), (6), (9), (10) and (15) show the domains of stability of Cu, Cu₂O, CuO and CuCl at Cl⁻ ion activities equal to $10^{-1}$, $10^{-2}$ and $10^{-3}$, and refer to the reactions between solid phases in the mixed solution. The additions of Cl⁻ ions enlarge the domain of predominance of CuCl, inversely, the domain of Cu₂O becomes narrower. These signify also that the reaction of equation (9) proceeds to the left side, and the resultant product, that is CuCl, on the base metal is stabilized. But this is incompatible with that the measured potentials in the case of $10^{-1}$ g-ion/$l$ Cl⁻ ions are recognizable in the domain of predominance of metallic Cu. The phenomena of the potential depression resulted from the

addition of Cl⁻ ions, accordingly, can't be explained by the reactions between the solid phases only in the mixed solution. Then, two solid phases Cu, CuCl and three solutes Cu⁺, Cu²⁺ and CuCl₂⁻ as complex ion in the mixed solution were examined in further consideration. **Figure 8** shows the effect of the potential on equilibrium activities of Cu⁺, Cu²⁺ and CuCl₂⁻ in contact with Cu and CuCl, when the Cl⁻ ion activity is $3.2 \times 10^{-2}$ as one example.
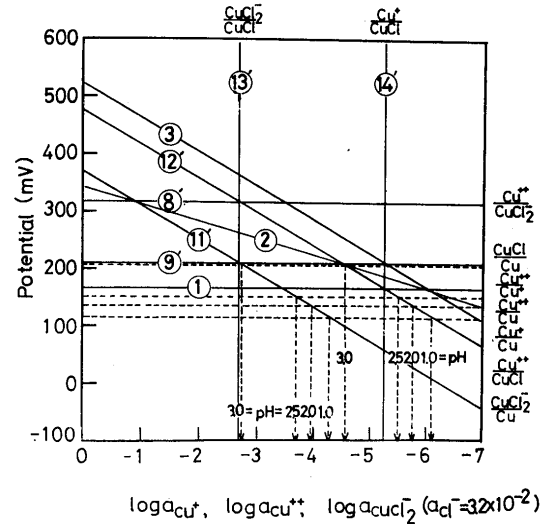


Fig. 8. Effect of potential on activity of Cu⁺, Cu²⁺ and CuCl₂⁻ ion in contact with Cu and CuCl.

The dotted number shows that the Cl⁻ ion activity of equation corresponded to the number is $3.2 \times 10^{-2}$. The broken lines show the potential values measured in the mixed solution of each pH with Cl⁻ ion activity of $3.2 \times 10^{-2}$, and the ordinates of these lines were drawed for convenience of illustration. The straight lines ⑫′ and ②, ⑬′ and ⑪′, and ⑭′ and ③ respectively intersect at a point of ordinate 212 mV : this is the standard potential for the CuCl/Cu equilibrium showed as the straight line ⑨′. Also, the straight lines ② and ⑪′ intersect at a point of ordinate 319 mV : this is the standard potential for the Cu²⁺/CuCl₂⁻ equilibrium showed as the straight line ⑧′, at which the concentrations of both ions are equal, and below which the complex ion CuCl₂⁻ is predominant. Each measured value belongs in this domain, furthermore except for the measured value of pH 3 all values lie below the straight line ①: this is the standard potential for the Cu²⁺/Cu⁺ equilibrium. These discussions, in conjunction with those given previously, made it possible to consider that the copper base metal in the mixed solution of pH 1 to 2.5 produced the complex ion CuCl₂⁻ owing to the left side proceeding reaction of equation (11). **Figure 9** shows a detail relation between the corrosion potential shown in Fig. 7 and
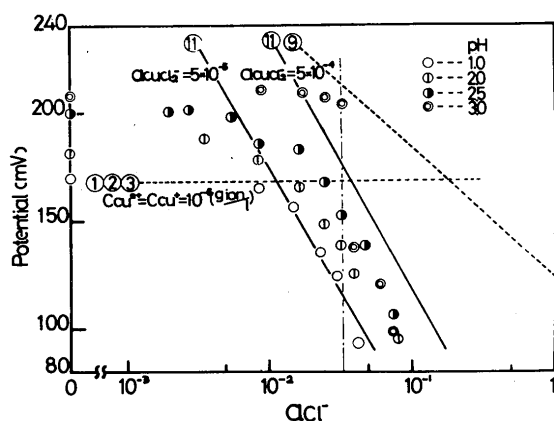
Fig. 9. Relation between corrosion potential of copper and activity of Cl⁻ ion in mixed flux aq. solution.

the activity of Cl⁻ ion in the mixed solution. The broken line with a dot shows the position of $a_{Cl^-} = 3.2 \times 10^{-2}$ utilized in Fig. 8. The potentials of pH 3 at this position are uncontinuous. As can be seen in Fig. 8, the straight lines ⑬′ and ⑨′ intersect at a point of ordinate 212 mV, which approximately coincides with the measured potential (that is 210 mV) of noble side on the uncontinuous curve. On the other hand, in Fig. 8, the straight lines ⑬′ and ① intersect at a point of ordinate 168 mV, which fairly coincides with the measured potential (that is 158 mV) of base side on the uncontinuous curve. This situation made it possible to consider that the uncontinuous phenomenon depended on the reaction of equation (13), which is independent of a electromotive reaction. It has been already described, as to the aqueous solution of $H_2SO_4$ of pH 3, that the $Cu_2O$ on the copper base metal will be formed by the right side proceeding reaction of equation (5). This $Cu_2O$, in the presence of Cl⁻ ion in the mixed solution, will be transformed to the CuCl owing to the right side proceeding reaction of equation (10), and in addition the $CuCl_2^-$ will be formed from the CuCl owing to the right side proceeding reaction of equation (13).

As can be seen in Fig. 9, when the activity of Cl⁻

ion is more larger than about $10^{-2}$, the potential of pH 1 decreases along a theoretical line of ⑪, at which the value of $a_{CuCl_2^-}$ is $5 \times 10^{-5}$. From this fact, the $a_{CuCl_2^-}$ values at each pH were calculated, inversely, by substituting the measured potential values for "E" of equation (11). The bottom side of Table 3 shows those values, and the top side shows the corresponding results obtained by using a graphical method in Fig. 8. The method is as follows: The first, in the diagram, a vertical broken line was drawed through a point, at which the line of ⑪′ and the broken line represented a measured potential value intersect. Consequently, the vertical line divides an axis of abscissa, as shown by an arrow, and a log $a_{CuCl_2^-}$ value to be desired can be obtained on this axis. As can be seen in the table, both values of pH 3 are very different. As mentioned already, the value obtained from Fig. 8 means the varying process from the reaction of equation (9) to one of equation (11). The value obtained from Fig. 9 means the varying process from the reaction of equation (1) to one of equation (11). Moreover, the table shows that the $a_{CuCl_2^-}$ values increase with an increasing of the pH value. This phenomenon can be attributed to the fact that $a_{CuCl_2^-}$ of equation (13) increases as pH of equation (10) increases.

Table 4 shows activity of $Cu^{2+}$ ion at each pH solution. Top side values are calculation values obtained from the measured values of Fig. 6 and "E" of equation (2). Bottom side values were obtained with the graphical method in Fig. 8, in which since the line of ⑫′ and the broken line denoted the measured value intersect, a log $a_{Cu^{2+}}$ can be obtained on the axis with the method mentioned already. From these values in the table, the effect of Cl⁻ ion on activity of $Cu^{2+}$ ion in the mixed solution is believed to be considerably small. On the other hand, the activity of $Cu^+$ ion is also possible to neglect because $a_{Cu^+}$ is about one over three hundred and eighty of $a_{CuCl_2^-}$, which can be calculated by substituting $a_{Cl^-} = 3.2 \times 10^{-2}$ for equation (7).

Table 3. Activity of $CuCl_2^-$ ion.

| pH | 1.0 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|
| $a_{CuCl_2^-}$ obtained from Fig. 8 | $2.6 \times 10^{-5}$ | $1.0 \times 10^{-4}$ | $2.0 \times 10^{-4}$ | $2.0 \times 10^{-3}$ |
| $a_{CuCl_2^-}$ obtained from Fig. 9 | $5.0 \times 10^{-5}$ | $1.0 \times 10^{-4}$ | $2.0 \times 10^{-4}$ | $2.0 \times 10^{-4}$ |

Table 4. Activity of $Cu^{2+}$ ion.

| pH | 1.0 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|
| $a_{Cu^{2+}}$ obtained from Fig. 6 | $1.0 \times 10^{-6}$ | $1.5 \times 10^{-6}$ | $1.2 \times 10^{-5}$ | $3.1 \times 10^{-5}$ |
| $a_{Cu^{2+}}$ obtained from Fig. 8 | $7.9 \times 10^{-7}$ | $1.5 \times 10^{-6}$ | $3.1 \times 10^{-6}$ | $2.5 \times 10^{-5}$ |

### 3.2.3 Relation between $\log a_{Cl^-}$ and pH of the mixed solution

We had reported in above paragraph that the uncontinuous phenomenon in the mixed solution of pH 3 (See Fig. 4) may be attributed to the reaction of equation (10). The relation between $\log a_{Cl^-}$ and pH of this equation is thus as shown in **Fig. 10.** In the figure, the unblank marks are the calculated $\log a_{Cl^-}$ that obtained by substituting the $\cdot a_{CuCl_2^-}$ values of top side in Table 3 for equation (13). The blank marks are the values of the limitting $Cl^-$ ion concentration observed in Fig. 4, whose values were converted justly to $\log a_{Cl^-}$. Through these marks, a line parallel to the straight line equation (10) can be drawed as shown in the figure. This line means a limit whether the solder does spread or doesn't, namely, the spreading is possible in the domain below this line and is impossible in the domain above this line. The equilibrium constant of this line can be obtained graphically as follows;

$$\log a_{Cl^-} = -4.65 + pH \quad (\text{where } 1 < pH < 3)$$

On the other hand, the equilibrium constant of equation (10) is $-5.82$. This discrepancy may be attributed to the fact that the system hasn't the CuCl at the initiation of immersion, and is unequilibrium. Now, when the pH of some flux solution is given, the minimum $Cl^-$ ion content necessary to spread the solder can be calculated from this equation. The broken line within the pH 2 curve in Fig. 4 shows the result that obtained by this equation. For the pH 1 curve also the limitting $Cl^-$ ion content can be obtained similarly, whereas the spread area of solder is about constant for $Cl^-$ ion concentration, and such suddenly increasing phenomenon does not produced in Fig. 4. From this fact it is belived that the $Cu_2O$, which prevents for spreading of solder and varies to CuCl by adding $Cl^-$ ion, is not existent on the surface of base metal in the pH 1 solution.
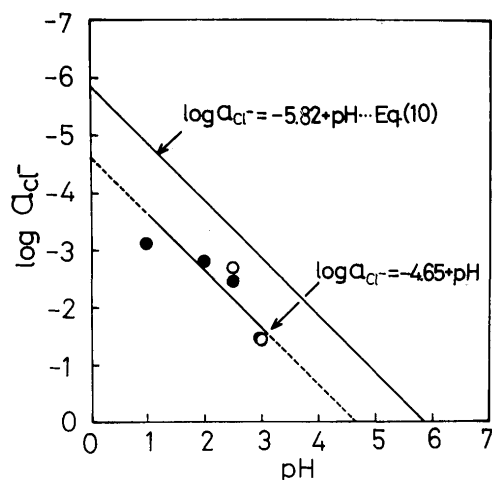


Fig. 10. Relation between $\log a_{Cl^-}$ and pH of flux aq. solution used.

### 3.3 Corrosion potential of solder in flux solution studied

The corrosion potential of solder in an aqueous solution of $H_2SO_4$ of each pH is shown in **Fig. 11.** Two dotted lines show the calculated values which obtained by substituting $C_{Cd^{2+}} = 10^{-3}$, $10^{-4}$ (where an activate coefficient assumes as one) for the logarithm term of equation (16)[3]. A full line shows equation (17)[3].

$$Cd^{2+} + 2e^- = Cd$$
$$E = -402 + 29.5 \log a_{Cd^{2+}} \quad \text{-----------------------(16)}$$

$$Cd(OH)_2 + 2e^- = Cd + 2OH^-$$
$$E = 19.3 - 59.1 \, pH \quad \text{------------------------------(17)}$$
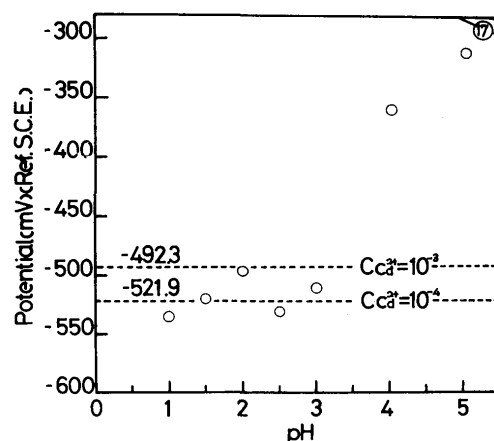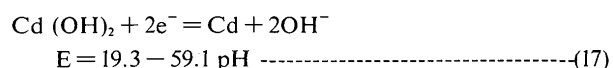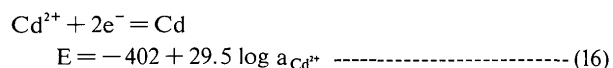


Fig. 11. Corrosion potential of solder in $H_2SO_4$ aq. solutions at 25°C.

The measured values in range from pH 1 to 3 lie between two dotted lines and in the case of pHs 4 and 5 approach to the line of equation (17). From these results it was considered that the corrosion reaction at pHs 1, 2 and 3 depends to the equation of (16) and at pHs 4 and 5 depends to the equation of (17). The former is called a hydrogen evolution type corrosion and the latter an oxygen consumption type corrosion. Accordingly, the cathode face on the solder surface is covered with $Cd(OH)_2$ and the $Cd^{2+}$ ion concentration front the anode face increases and the metal potential becomes to rise. The noble potential means that the solder is covered with thicker $Cd(OH)_2$ and is passivated. This passivative state of solder may be considered as the reason that the spread area of solder at pHs 4 and 5 shown in Fig. 3 does not occurred. The limitation of this passivation is considered to be pH 3 from the figure. The other hand, the effect of the oxide, $Cu_2O$, on the surface of base metal for the spreading of solder, as mentioned already, becomes remarkably at $H^+$ ion concentration lower than pH 1. It is concluded accordingly that the spreading of solder

studied depends on the surface condition of base metal, although the solder has a possibility to spread in the flux solution.

**Figure 12** shows the effect of $Cl^-$ ion added to the pH 2.5 solution as one example on the corrosion potential of solder. The potential decreases with an increasing of $Cl^-$ ion concentration. This phenomenon agrees with the result in Fig. 9, but the mechanic of depression is not evident as that of Fig. 9, because thermodynamical data of $CdCl_2$ are little. Anyhow, it would be true that $CdCl_2$ or $Cd(OH)_2$ dissolves to the solution containing $Cl^-$ ion and the solder is stable in the solution.
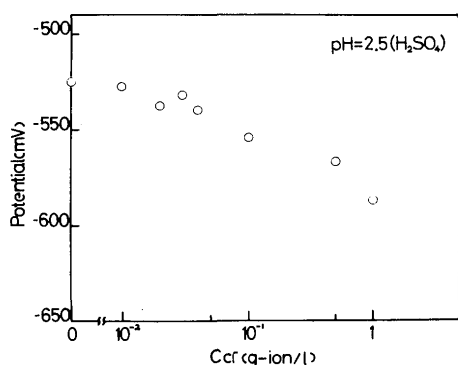


Fig. 12. Relation between corrosion potential of solder and concentration of $Cl^-$ ion in mixed flux aq. solution.

## 4. Conclusions

The conclusions obtained through the experiments and considerations are as follows:

1) The flux actions of $H^+$ and $Cl^-$ ions for spreading of solder used on copper base metal have been considered electrochemically.

2) The flux action of $H^+$ ion is exhibited by the reaction of equation (4), and the spread area of solder increases with an increasing of $H^+$ ion concentration in the solution used. The oxide, $Cu_2O$, formed on the surface of base metal prevents for spreading of the solder.

3) The flux action of $Cl^-$ ion is given by the reactions of equations (10) and (13), namely, the $Cu_2O$ is chloridized to $CuCl$ and moreover is complex-ionized to $CuCl_2^-$ ion. Accordingly, the spreading of solder occurs suddenly at some $Cl^-$ ion concentration (See Fig. 4).

4) A quantitative relation, which denotes a critical condition whether the solder does spread or doesn't, between $Cl^-$ ion and $H^+$ ion in the flux solution was obtained experimentally as follows:

$$\log a_{Cl^-} = -4.65 + pH \qquad \text{(where } 1 < pH < 3)$$

When pH is given, the $Cl^-$ ion concentration higher than that is obtained from above equation is necessary for spreading of solder used.

5) The spreading of solder was considered to be depended rather the surface condition of base metal than that of solder affected by the flux solution containing $Cl^-$ and $H^+$ ions.

## Acknowledgement

**References**

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