Title	Selection of Optimum Cu Content in Cu Bearing Tin-Lead Solder(Materials, Metallurgy & Weldability)
Author(s)	Okamoto, Ikuo; Yasuda, Tomio
Citation	Transactions of JWRI. 1986, 15(2), p. 245-252
Version Type	VoR
URL	https://doi.org/10.18910/11711
rights	
Note	

Selection of Optimum Cu Content in Cu Bearing Tin-Lead Solder†

Ikuo OKAMOTO* and Tomio YASUDA**

Abstract

Dissolution rate of copper in a molten 60Sn-40Pb solder was theoretically studied. The rate constant was calculated using the experimental data and physical constants. The temperature dependence of the rate constant, namely, the apparent activation energy of dissolution was 0.17 eV/atom. The rate constant in a molten 60Sn-40Pb solder containing previously added copper was also calculated through the same process, and the relation between these two rate constants with and without copper addition was made clear. According to the comparison of calculated values with measured ones, it was proved that the dissolution of a fine copper wire can be well approximated by the semi-experimental equation when the volume of the molten solder was large enough compared with that of the fine copper wire. Besides, 60Sn-40Pb/Cu quasibinary eutectic solder (0.23 wt% Cu) was proposed as the means to minimize the erosion of fine copper wires in the molten solder.

It was proposed that the initial dissolution rate of a fine copper wire was given as the mathematical product of the rate constant of dissolution and the equilibrium solubility of copper in a molten solder. The apparent activation energy was determined to be 0.48 eV/atom.

KEY WORDS: (Soldering) (Erosion) (Copper) (Tin-Lead Solder) (Microbonding)

1. Introduction

One of the main concerns in microbonding technology is the reliability of the joint strength of the interconnections. Since the device (silicon) and substrate (ceramic) are both nonmetallic and nonwettable by tin-lead solder, so called metallization of the device and substrate are essential in order to ensure the formation of mechanically sound and electrically conductive joints by tin-lead solder. Most of the metallization processes are those by the screen printing or vapour deposition technique, and they give a thin metal film sensitive to erosion by tin-lead solder of the order of 10 to 10^{-1} microns (Fig. 1).

There have been useful investigations on the dissolution phenomena of copper in a molten solder,[1-5] where the dissolution rate constants are empirically determined. And, addition of a small quantity of the element of the thin metal film to tin-lead solder is proposed and widely utilized in the electronics industry, but the concentration of the element has only been determined empirically
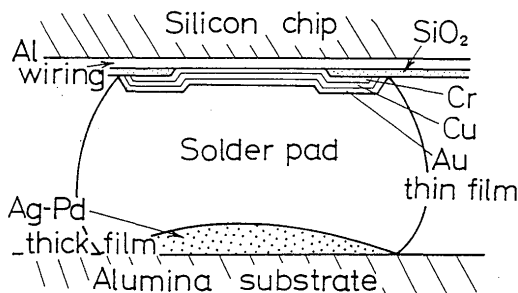
without any theoretical considerations.

This article is devoted to discussing the theoretical determination of the optimum content of the added element, especially copper, in tin-lead solder for a soldering technique of the copper thin film by tin-lead solder.

To begin with, the theoretical concept of erosion of a solid by a liquid will be introduced.

2. Theoretical Background

Figure 2 shows a model of solution phenomenon of solid into liquid. For the solution phenomenon of solid metal (ex. copper) into liquid metal (ex. tin-lead solder), equation (1) is given as follows.[6]

$$\frac{dS}{dt} = K \frac{A}{V_0} (S^0 - S) \tag{1}$$

where,

S : Concentration of solid in liquid (g/cm^3)
S^0 : Equilibrium solubility at temperature, T (g/cm^3)
K : Specific solution rate constant (cm/s)
A : Area of the solid-liquid interface (cm^2)
V_0 : Volume of liquid (cm^3)
t : Time (s)

For the copper, fine round wires were used in the experiment (see Fig. 4), and also as it is convenient to use molar fraction instead of weight % for theoretical treatment, the equation (1) should be modified.

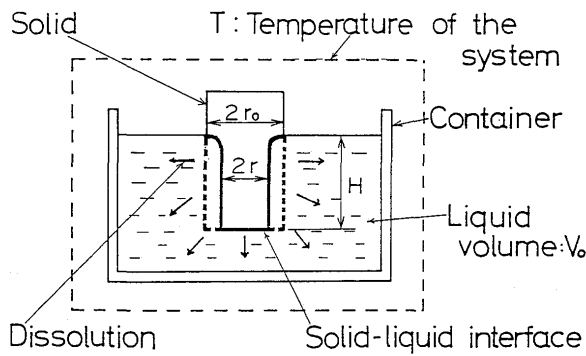

Fig. 1 Example of microbonding.

Fig. 2   Schema of solution phenomenon of solid into liquid.

Assuming the radius of a Cu wire to be r at time t, the interface area A between Cu wire and solder is,

$$A = 2\pi r H \tag{2}$$

where, H is the length of the dipped part of the Cu wire in solder, and is constant throughout measurement (see Fig. 4). The dissolved volume of Cu wire, dV (cm^3) during the time dt is expressed by the decrement of radius, dr,

$$dV = -A dr \tag{3}$$

The dissolved quantities of Cu wire, dm (mol) in the time dt will then be

$$dm = \frac{\rho_1 dV}{M_1} = -\frac{\rho_1 A dr}{M_1} \tag{4}$$

where, ρ_1 and M_1 are density and atomic weight of copper respectively. The concentration increment dC (molar fraction) in the time dt is

$$dC = \frac{dm}{\rho_2 V_0 / M_2} = \frac{M_2}{M_1} \frac{\rho_1 dV}{V_0} \frac{1}{\rho_2} = M\rho \frac{dV}{V_0}$$

$$= -\frac{M\rho A dr}{V_0} \tag{5}$$

where, ρ_2 and M_2 are density and atomic weight of solder and the volume of solder is assumed to be large enough compared to that of dissolved Cu. And $M = M_2/M_1$, $\rho = \rho_1/\rho_2$ are defined. The atomic weight M_2 is defined here,

$$M_2 = M_s \times A_s + M_p \times A_p \tag{6}$$

where, M_s and M_p are the atomic weight of tin and lead respectively, and A_s and A_p are the atomic percentage of tin and lead respectively.

Considering the relation of the third term of equation (5) and dS (g/cm^3) $= \rho_1 dV/V_0$,

$$dS = \frac{\rho_2}{M} dC \tag{7}$$

$$\frac{dS}{dt} = \frac{\rho_2}{M} \frac{dC}{dt} \tag{8}$$

From the assumption of a large solder volume, the density and atomic weight of solder may be taken constant even after the dissolution of the Cu wire. And then, equation (8) gives

$$S = \int_0^t dS = \frac{\rho_2}{M} \int_0^t dC = \frac{\rho_2}{M} C \tag{9}$$

From equations (2) and (5),

$$C = \int_0^t dC = -\frac{M\rho}{V_0} \int_{r_0}^r A dr = -\frac{\pi M\rho H}{V_0} \int_{r_0}^r 2r dr$$

$$= -\frac{\pi M\rho H}{V_0} (r^2 - r_0^2) \tag{10}$$

where, $2r_0$ is the initial diameter of Cu wire.

Equilibrium solubility S^0 at temperature T is converted into that in molar fraction C_s, from equation (9),

$$S^0 = \frac{\rho_2}{M} \cdot C_s \tag{11}$$

Equation (1) can be rewritten and arranged with the relations (5), (8), (9), (10) and (11),

$$\frac{dr}{dt} = \frac{K}{M\rho} \left\{ (\frac{\pi \rho M H r_0^2}{V_0} - C_s) - \frac{\pi \rho M H}{V_0} r^2 \right\} \tag{12}$$

Equation (12) is a simple variable-separated type differential equation and yields three different solutions accordingly if the term in the parentheses is positive or negative.

$$(\frac{\pi \rho M H r_0^2}{V_0} - C_s) = \beta^2 > 0$$

The solution is

$$ln \left(\frac{1 - \frac{\lambda}{\beta} r}{1 + \frac{\lambda}{\beta} r} \right) = ln \left(\frac{1 - \frac{\lambda}{\beta} r_0}{1 + \frac{\lambda}{\beta} r_0} \right) - \frac{k\beta\lambda}{M\rho} t \tag{13}$$

where,

$$\beta = \sqrt{\frac{\pi \rho M H r_0^2}{V_0} - C_s} \quad , \quad \lambda = \sqrt{\frac{\pi \rho M H}{V_0}}$$

$$(\frac{\pi \rho M H r_0^2}{V_0} - C_s) = \beta^2 = 0$$

$$\frac{1}{r} = \frac{1}{r_0} + \frac{K\pi H}{V_0} t \tag{14}$$

$$\left(\frac{\pi \rho M H r_0^2}{V_0} - C_s\right) = -\beta^2 < 0$$

$$tan^{-1}\left(\frac{\lambda}{\beta}r\right) = tan^{-1}\left(\frac{\lambda}{\beta}r_0\right) - \frac{K\beta\lambda}{M\rho}\,t \qquad (15)$$

where,

$$\beta = \sqrt{C_s - \frac{\pi \rho M H r_0^2}{V_0}}\quad,\quad \lambda = \sqrt{\frac{\pi \rho M H}{V_0}}$$

The curves obtained from equations (13), (14) and (15) are plotted in **Fig. 3**, by substituting several data of the experiment explained later and of references.[7-9]

Equation (14) corresponds to the condition where the mass of copper wire immersed under the surface of molten solder is equal to the copper content of the equilibrium solubility at the temperature. Equation (13) corresponds to the excess mass of copper wire and equation (15) to the too little mass of it, compared with the mass of the molten solder.

In this experiment, the copper wires were thin enough comparing with the solder volume to adopt equation (15) for explaining the experimental data.
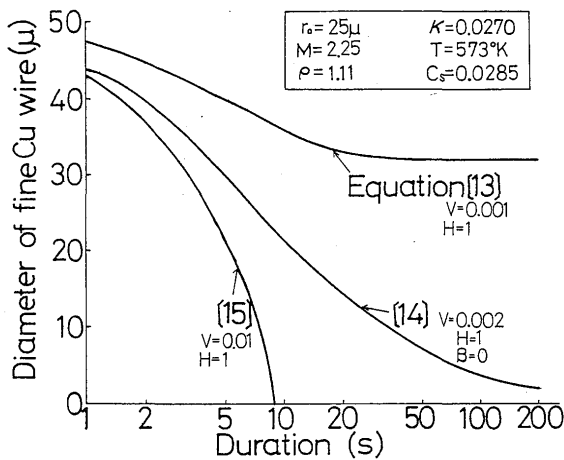

Fig. 3 Dissolution curves expressed by equations (13), (14) and (15).

3. Experimental Procedure

The copper 50μ dia. wires used were oxygen free, and the solder with composition of 60 weight % tin and 40 weight % lead was prepared from virgin ingots of 99.95% tin and 99.99% lead.

For measurement of destruction time, the method developed by C. A. Harrison was adopted as shown in **Fig. 4**.[10] Preformed U-bends of fine copper wires were dipped in the molten solder to permit the free ends of the U-bends to remain out of the solder to 1/2 its length. The time from the moment of entry into the solder to the moment of falling over due to the erosion by solder was
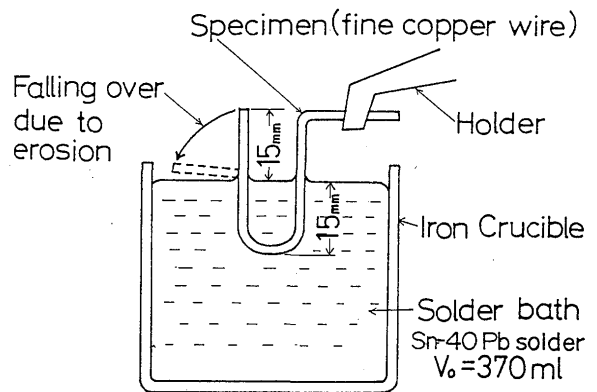

Fig. 4 Apparatus for measurement of destruction time of fine copper wire.

measured as the destruction time, t_E. When this vertical projection fell over, it was assured that almost all the section of wire had been eaten away thus making it incapable of supporting even this small weight.

4. Results and Discussions

4.1 Destruction time measured using two kinds of solder

Results for 60 : 40 tin-lead solder are shown in **Tables 1** and **2**. As seen in both tables, solder containing previously added Cu prevents to a great extent the erosion of Cu wire by solder.

According to the results of thermal analysis of copper

Table 1 Destruction time, t_E (s) measured with 60Sn-40Pb solder.

Solder bath temperature (K)	Radius of fine copper wire, r_0 (cm)		
	2.5×10^{-3}	3.0×10^{-3}	3.5×10^{-3}
473	62.5	86.2	115
508	28.5	39.4	52.6
523	20.5	28.2	37.8
573	8.1	11.2	15.0
623	3.7	5.1	6.8
673	1.9	2.6	3.5

Table 2 Destruction time, t_E^* (s) measured with copper bearing 60Sn-40Pb solder.

Solder bath temperature (K)	Content of previously added copper, C_0 (wt%)			
	0	0.15	0.5	0.9
573	7.8	12.0	50.0	>200
623	4.0	5.5	8.3	15.0
673	2.0	2.6	2.9	3.8

$r_0 = 2.5 \times 10^{-3}$ cm

bearing 60 : 40 tin-lead solder, the liquidus curve of quasi-binary diagram of the solder, C_s is plotted against temperature T in **Fig. 5**.
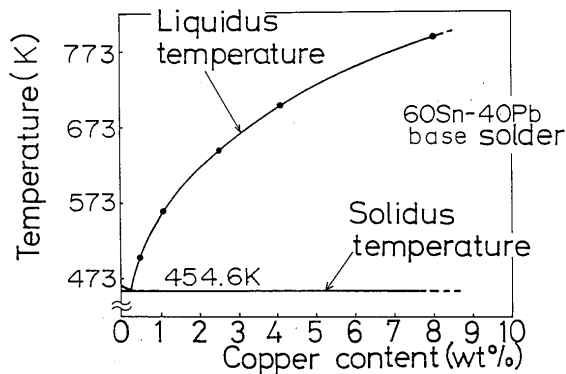

Fig. 5   Quasi-binary diagram of 60Sn-40Pb base solder.

4.2 Effect of soldering temperature on erosion of fine copper wire

Effect of soldering temperature appears in K and S^0 of equation (1). K is a function of temperature T (K) and may be expressed with constants K_0 and B as follows,

$$K = K_0 \exp\left\{ - B/RT \right\} \qquad (16)$$

R: Gas constant

Besides, S^0 is equivalent to C_s expressed in molar fraction as shown in equation (11). And then, C_s of equilibrium solubility, which is equal to the liquidus composition at a given temperature, should be given as a function of temperature. Fig. 5 yields equation (17) in Arrhenius expression as expected from thermodynamic theory.[11]

$$C_s = 15.4 \exp\left\{ -7150/RT \right\} \qquad (17)$$

$$(C_s \geqslant 5.21 \times 10^{-3}, T \geqslant 454.6\text{K})$$

On the other hand, from equation (15), rate constant K is expressed as follows,

$$K = \frac{M\rho}{t_E \beta \lambda} \, tan^{-1} \left(\frac{\lambda}{\beta} r_0\right) \qquad (18)$$

where,

$$\beta = \sqrt{C_s - \frac{\pi \rho M H r_0^2}{V_0}} \ , \quad \lambda = \sqrt{\frac{\pi \rho M H}{V_0}}$$

As $tan^{-1}x$ nearly equals x for small x, that is $\lambda \cdot r_0/\beta \ll 1$, equation (18) can be rewritten as equation (19) below.

$$K = \frac{M\rho r_0}{t_E \left\{ C_s - \Sigma \right\}} \qquad (19)$$

where,

$$\Sigma = \frac{\pi \rho M H r_0^2}{V_0}$$

Substituting the data from Table 1 and equation (17) for t_E and C_s in equation (19), K can be calculated also with several parameters shown in **Table 3**. Arrhenius expression of calculated K (in **Fig. 6**) yielded the value of 3890 cal/mol (0.169 eV/atom) for B in equation (16), and K_0 shown in **Table 4**.

From the data in Table 4, K_0 obviously depends on diameters and hence radii of copper wires. K_0's dependence on r_0 was numerized according to the fact that K_0 was approximately proportional to the reciprocal of r_0 as shown in **Fig. 7**. Therefore, equation (16) is finally rewritten as equation (20) below.

Table 3   Parameters used to calculate K from equation (19).

Parameter	Value
ρ	1.09 (473K), 1.10 ($\leqq$ 523K) 1.11 ($\leqq$623K), 1.12 (673K)
M	2.253
H (cm)	3.00
V_0 (cm³)	3.70×10^2
r_0 (cm)	$2.5 \times 10^{-3}, 3.0 \times 10^{-3}, 3.5 \times 10^{-3}$

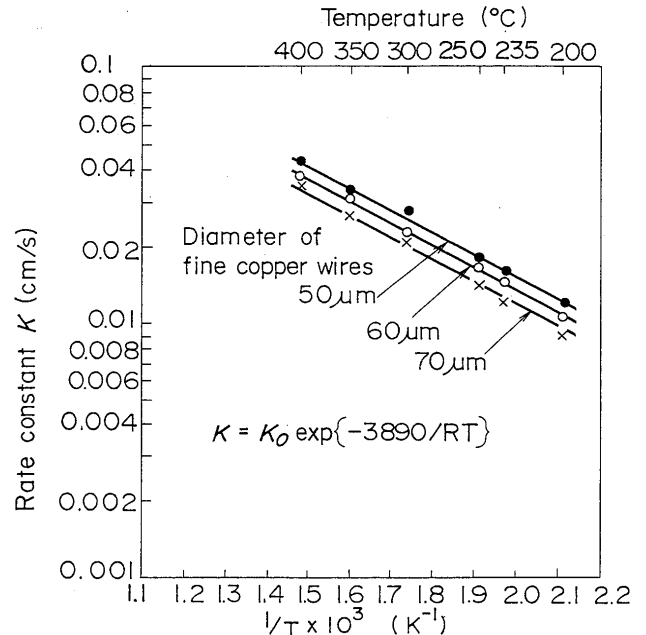**Fig. 6**   Arrhenius expression of rate constant, K.

Table 4 K_0 obtained from Fig. 6.

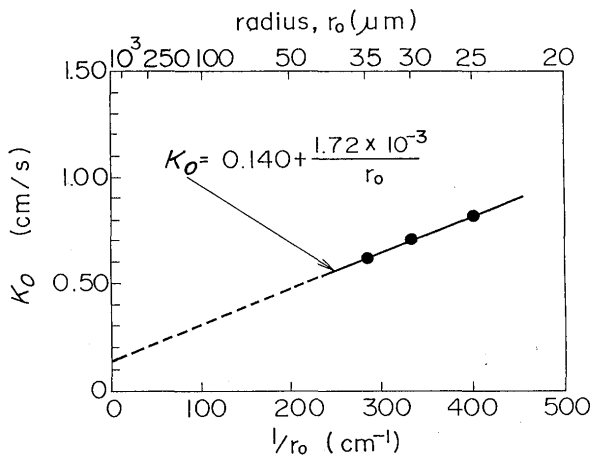| Diameter of copper wire (cm)	K_0 (cm/s)
5.0×10^{-3}	0.826
6.0×10^{-3}	0.719
7.0×10^{-3}	0.625

Fig. 7 Dependence of K_0 on reciprocal of r_0, radii of copper fine wires.

$$K = (0.140 + \frac{1.72 \times 10^{-3}}{r_0}) \exp \left\{ -3890/RT \right\} \quad (20)$$

The reason for r_0 dependence of K_0 may be due partially to the temperature fall of a molten solder adjacent to specimens when they are dipped in it.

In this experiment, r_0 is sufficiently small comparing with V_0 and then Σ in equation (19) may be ignored. The physical meaning of nullification of Σ for C_s is that the dissolution of the total mass of immersed copper is small enough to be nullified in comparison with the equilibrium solubility C_s at the temperature in question. Consequently, equation (19) is rewitten as equation (21).

$$t_E = \frac{M\rho r_0}{K \cdot C_s} \quad (21)$$

Combining equations (17), (20) and (21), destruction time t_E of fine copper wire can be calculated for the temperature range from 473K to 673K. Comparison of experimental data with calculated values from equation (21) combined with semi-experimental equations (17) and (20), is shown in **Fig. 8**. They agree rather well with each other and equation (21) is proved to express substantially the effect of soldering temperature on erosion of fine copper wire.

It may not be meaningless to indicate that $K_0 = 0.140$ at $1/r_0 = 0$ in Fig. 7. This means K_0 takes the value of 0.140 cm/s when r_0 reaches infinity. (i.e., when the specimen is not a round wire but a plate.) There still remains more experimental work in order to assure if 0.140 corresponds the value of K_0 for the copper plate or film with plane surface.

It must be pointed out that equation (21) is only valid when the dissolution of copper wire does not result in considerable increase of copper content in solder bath, compared with the equilibrium solubility of copper in the molten solder.
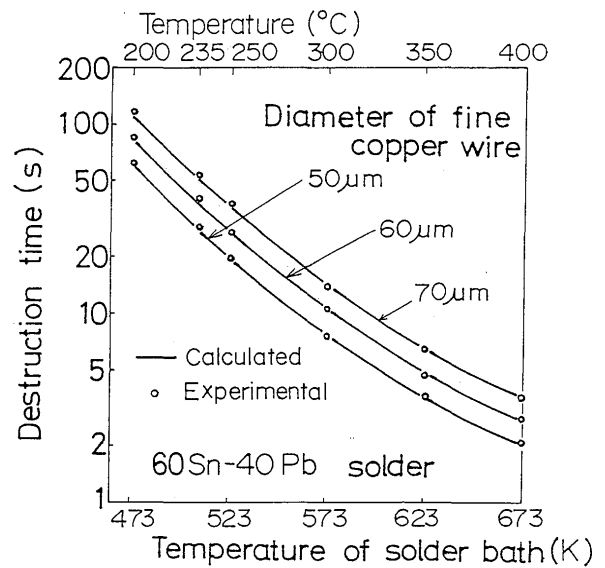

Fig. 8 Erosion of fine copper wire by 60Sn-40Pb molten solder.

From equation (12), the initial dissolution rate can be induced by substituting the relation, $r = r_0$ at $t = 0$, as follows.

$$(\frac{dr}{dt})_{t=0} = -\frac{KC_s}{M\rho} \quad (22)$$

By substituting equations (17) and (20), equation (22) yields equation (23).

$$(\frac{dr}{dt})_{t=0} = -15.4 \frac{K_0}{M\rho} \exp \left\{ -3890/RT \right\} \cdot$$

$$\exp \left\{ -7150/RT \right\}$$

$$= -15.4 \frac{K_0}{M\rho} \exp \left\{ -11040/RT \right\} \quad (23)$$

The apparent activation energy of 11040 cal/mol (0.48 eV/atom) in equation (23) is about 10% smaller than 12500 cal/mol by Bader, who measured the dissolution rate of copper wire in a molten 60Sn-40Pb solder and gained the linear dissolution rate, i.e., the initial dissolution rate.[2] This 10% discrepancy may be due to limitations in the test procedure, e.g., flux evaporation, temperature fall, etc.

4.3 Effect of copper addition in molten solder on erosion of fine copper wire

Effect of copper addition to solder can be anticipated qualitatively from equation (1), and deduced quantitatively from equation (12). In equation (10), the previous addition of copper means modification of the term $\int_0^t dC$ to $\int_0^t dC + C_0$, where C_0 is the amount of previously added Cu in solder. From equation (12), the decreasing rate of the radius of Cu wire can be calculated by

substituting the term $(C_s - C_0)$ in place of C_s.

From equation (19), destruction time t_E is expressed as follows,

$$t_E = \frac{M \rho r_0}{K \left\{ (C_s - C_0) - \Sigma \right\}} \qquad (24)$$

where,

$$\Sigma = \frac{\pi \rho M H r_0^2}{V_0}$$

The data from Table 2 indicates that the previous addition of copper into solder reduces erosion of copper wires and increases destruction time t_E^* significantly. However, experimental values of t_E^* were quite different from those calculated using equations (17), (20) and (24). The authors assumed that K in equation (24) might be dependent on C_0, the content of previously added copper, while it was dependent on diameter of copper wire.

K^*, rate constant for erosion of fine copper wire in copper bearing molten solder, is obtained by substituting t_E^* in Table 2 into equation (24). The ratios of K^* to K which was the value obtained by calculating equations (17), (19) and (20), were taken logarithm of themselves and were plotted against C_0, the content of previsouly added copper in the molten solder, in **Fig. 9.** The logarithm of K^*/K seems to be a linear function of C_0, but the gradient of each straight line is dependent on soldering temperature.

$$ln \ (K^*/K) = -m(T) \cdot C_0 \qquad (25)$$

The gradients, m of 3 lines in Fig. 9 are plotted in **Fig. 10** against the reciprocal of absolute temperature of soldering. They plot as a straight line when logarithm of m is taken.

Finally, equation (26) is obtained.

$$ln \ (\frac{K^*}{K}) = -7.00 \times 10^{-3} \cdot exp \ (5550/T) \cdot C_0 \qquad (26)$$

where, K is obtained from equation (20).

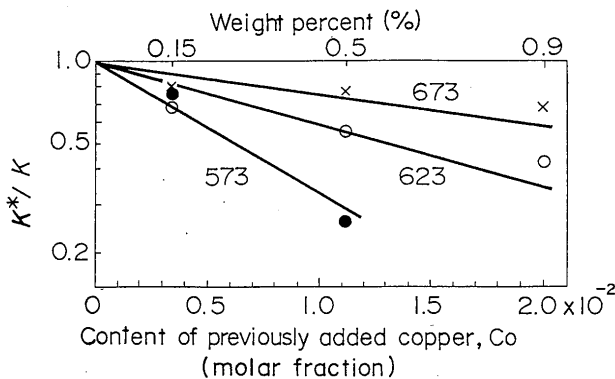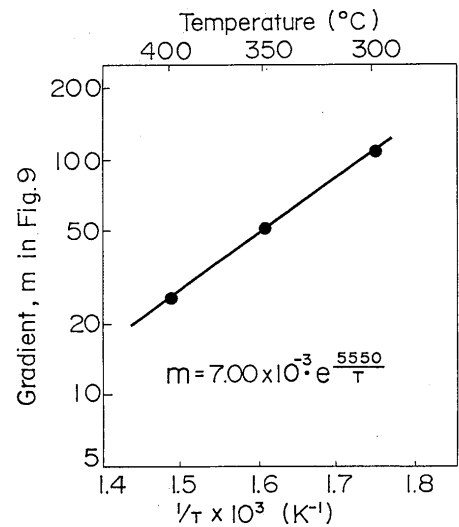**Fig. 10**   Temperature dependence of gradients of lines in Fig. 9.

Substituting K^* from equation (26) into equation (24), destruction time t_E^* with copper bearing 60 : 40 tin-lead solder is written as equation (27), assuming $\Sigma \ll C_s - C_0$.

$$t_E^* = \frac{M \rho r_0}{K^* \cdot (C_s - C_0)} \qquad (27)$$

Good agreement of the values calculated from equation (27) with the experimental values in Table 2 is shown in **Fig. 11.**

Physical meaning of equation (26) is not yet recognized by the authors. The previous addition of copper only affects K^*/K not at higher temperatures but at lower temperatures. This fact may suggest the orderliness of copper atoms near the copper wire/molten solder interface at lower temperatures. At least, the effect of previous addition of copper on K^* is well described by the experimental equation (26).
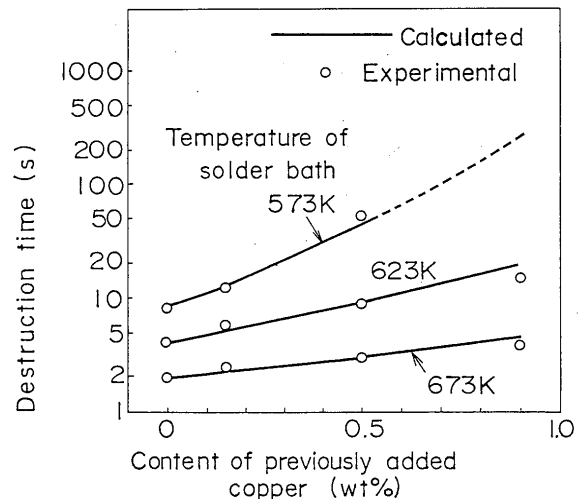

Fig. 9   Effect of copper content and temperature on logarithm of K^*/K.

Fig. 11   Effect of copper content in 60 Sn-40 Pb solder on erosion of 50μm dia. copper wire.

4.4 Reasonable selection of the optimum copper content in solder

As shown in Fig. 11, the destruction time t_E^* increases, i.e., the dissolution rate decreases, highly as the contents of previously added copper in a molten solder increase when the temperature of the molten solder is kept constant during the soldering operation. However, the higher the copper content in solder is, the higher the liquidus temperature of solder becomes. Since soldering temperature is usually chosen at a given temperature 30 to 50K higher than the liquidus temperature, soldering temperature must be raised corresponding to increase of the copper content in solder. The higher soldering temperature will results in enlargement of K^*, whose increase brings decrease of the destruction time t_E^*.

From equation (27) with equations (17), (20) and (26), t_E^* is given as a function of the super-heat ΔT, the temperature gap between the liquidus temperature of copper bearing solder and soldering temperature, in **Fig. 12**, which shows the optimum copper content of about 0.23 weight percent, i.e., the eutectic composition in 60Sn-40Pb/Cu quasi-binary phase diagram.

Calculation of the curves of t_E^* in Fig. 12 was made as follows (**Fig. 13**): First of all, super-heat ΔT was given and

then soldering temperature T^* was decided for the given content of previously added copper in solder C_0, the liquidus of which is T_L.

$$T^* = T_L + \Delta T \tag{28}$$

Then, C_s was calculated by substituting T^* into equation (17). K^* was also calculated by substituting T^* and C_0 into equations (20) and (26). t_E^* was obtained from equation (27) with C_0, C_s and K^*.

In Fig. 13 (i.e. Fig. 5), the liquidus curve less molar fraction of Cu than 5.21×10^{-3} (< 0.23 wt%) was expressed in equation (29) assuming the linear approximation.

$$C_s = 7.87 \times 10^{-4} (461 - T_L) \tag{29}$$

where,

$$C_s < 5.21 \times 10^{-3}$$

The value of C_0, 0.23 wt% can be called the optimum Cu content, because copper additions up to 0.5% in to a molten 60Sn-40Pb solder had very little influence on the
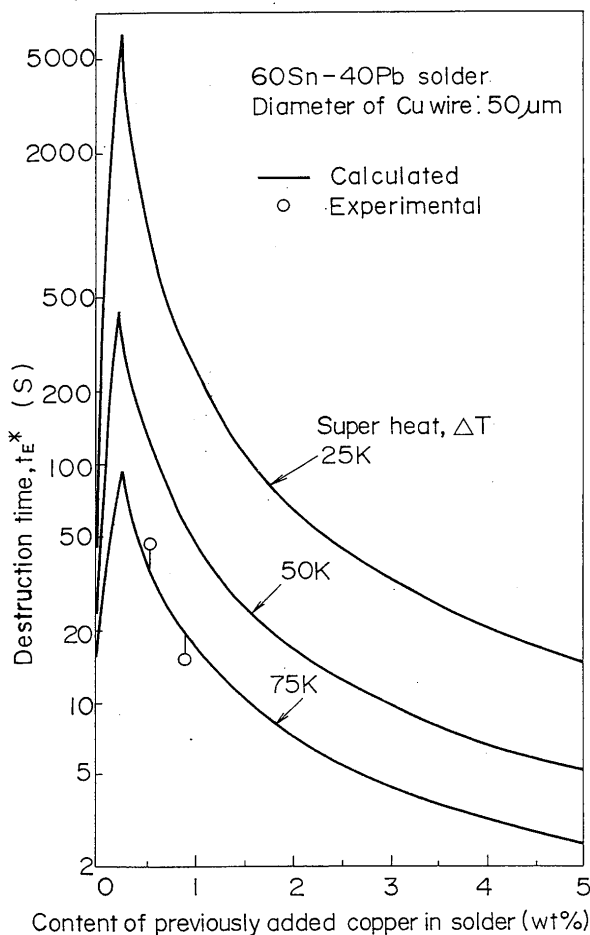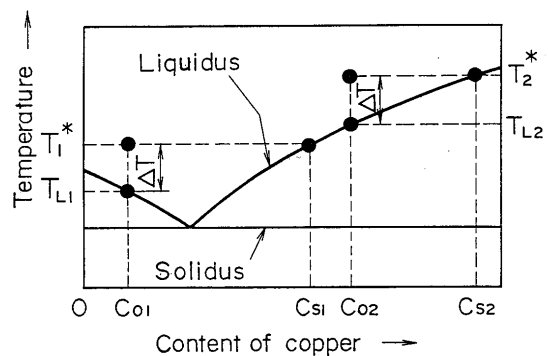

Fig. 13 Reference diagram explaining calculation process of t_E^* in Fig. 12.

Fig. 12 Selection of optimum copper content.

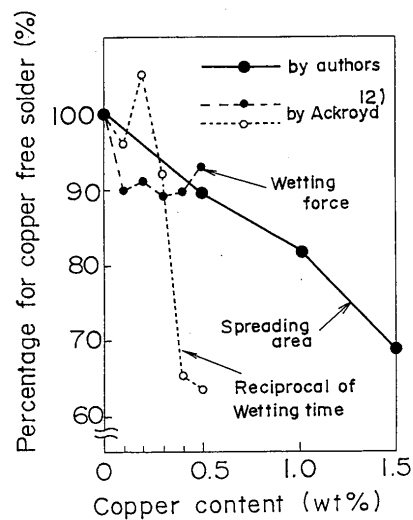**Fig. 14** Effect of copper content on wettability of 60Sn-40Pb solder on copper base metal.

wetting properties, according to M. L. Ackroyd et al.[12] and the author's experiment, Fig. 14.

5. Conclusions

The dissolution rate of copper fine wires in a molten 60Sn-40Pb solder was theoretically studied, and the way of determination of the optimum copper content in copper bearing tin-lead solders was proposed.

(1) The temperature dependence of the rate constant, namely, the apparant activation energy of dissolution was determined to be 0.17 eV/atom (3890 cal/mol).

(2) The temperature dependence of the equilibrium solubility of copper in a molten 60Sn-40Pb solder was determined to be 0.31 eV/atom (7150 cal/mol) as in equation (17).

(3) It was proposed that the initial dissolution rate was given as the mathematical product of the rate constant of dissolution and the euqilibrium solubility of solid (copper) in a molten metal (solder) and some other parameters, as in equation (22). The temperature dependence of the initial dissolution rate was determined to be 11040 cal/mol (0.48 eV/atom), which was about 10% smaller than 12500 cal/mol obtained by Bader.[2]

(4) The rate constant in a molten 60Sn-40Pb solder containing previously added copper was also induced using the experimental data and physical constant. The relation between the two rate constants with and without copper addition was made clear as in equation (26).

(5) The dissolution of a fine wire in a molten 60Sn-40Pb solder was proved to be well approximated by the induced semi-experimental equation (27) when the volume of the molten solder was large enough compared with that of the fine copper wire.

(6) The 60Sn-40Pb/Cu quasi-binary eutectic solder (0.23 wt% Cu) was proposed as the means to minimize the erosion of fine copper wires in molten 60Sn-40Pb solders.

References

1) M. A. R. Howes and Z. P. Saperstein: "The Reaction of Lead-Tin Solders with Copper Alloys" Weld. J. Vol. 48 (2) 1969, 80$_s$-85$_s$.

2) W. G. Bader: "Dissolution of Au, Ag, Pd, Pt, Cu and Ni in a Molten Tin-Lead Solder" Weld. J. Vol. 48 (12) 1969, 551$_s$-557$_s$.

3) T. Yasuda: "Selection of the Optimum Cu Content in Cu Bearing Tin-Lead Solder" Proceedings of the 2nd International Symposium of the Japan Welding Society, OSAKA, 25-28 August, 1975.

4) W. G. Bader: "Lead Alloys for High Temperature Soldering of Magnet Wire" Weld. J. Vol. 54 (10) 1975, 370$_s$-375$_s$.

5) Y. Shoji, et al.: "Dissolution of Solid Copper in Molten Tin-Lead Alloys under Static Conditions" Trans. of Japan Inst. of Metals Vol. 21 (12) 1980, 819-823.

6) Am. Inst. of Chem. Engrs: "Liquid Metals Technology Part I" 1957.

7) L. L. Bircumshaw: Phil. Mag. and J. Science (1934) 181.

8) Max Hansen: "Constitution of Binary Alloys" (1958).

9) Briesemeister: Z. Metallkunde (1931) 225.

10) C. A. Harrison: Metal Progress (1945) 282.

11) O. Kubaschewski, et al.: "Metallurgical Thermochemistry" 4th Edition (1967) 57-59 Pergamon Press.

12) M. L. Ackroyd, et al.: "Effect of Certain Impurity Elements on the Wetting Properties of 60% Tin-40% Lead Solders" Metals Technology (Feb. 1975) 73-85.