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Author(s)	Okamoto, Ikuo; Omori, Akira; Den, Koichi; Tamaki, Katsuomi
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Relation Between Spreading Area and Penetration Height in Soldering †

— On Wetting —

Ikuo OKAMOTO*, Akira OMORI*,* Koichi DEN*** and Katsuomi TAMAKI****

Abstract

The discrepancy in both tests of the spreading and the penetration of Pb-Sn solders in contact with copper plates was researched in this investigation. From the results obtained, it is evident that the discrepancy can be attributed to the fact that the surface (interfacial) tension of pure tin is greater than that of solder of near eutectic composition.

1. Introduction

It is well known in soldering that the maximum spreading of Pb-Sn solders on heated copper plates is obtained at near eutectic composition of the solders and the maximum equilibrium rising height of the solders in vertical capillary copper joints or the highest effective penetration coefficient of the solders in horizontal capillary copper joints is obtained respectively at pure tin in the composition of the solders. These phenomena were pointed from 1946 to 1951 out by A. Latin¹⁾ and G.L.J. Bailey et al²⁾, and as the cause of discrepancy, they have reported "hysteresis" of contact angles formed between the solders and copper plate. In particular, A. Latin has mentioned that the "imbibition" of the intermediate range of solders appears to be greater than that of tin-rich or lead-rich solders, and also G.L.J. Bailey et al have concluded that the flow of solder is controlled by the product of liquid surface tension and the cosine of the contact angle in capillary penetration, whereas in spreading on a plane surface, the area covered depends solely on the value of the contact angle.

The authors also had an interest for these phenomena and considered the discrepancy from a point of view of thermodynamic wetting between the solders and copper plate.

2. Calculation of wetting

When a liquid droplet contacts to a smooth solid

surface, the surface energy change at liquid-solid interface is given by eq. (1);

$$\sigma_s - \sigma_i \equiv A \quad (1)$$

where σ_s is the surface tension of solid before contact, σ_i is the interfacial tension at liquid-solid interface after contact, A is surface energy change, that is, wetting.

In above equation, σ_s and σ_i can not be measured directly at present. Then, Young-Duprès equation that shown in eq. (2) is used generally under equilibrium condition;

$$\sigma_s = \sigma_l + \sigma_l \cos \theta \quad (2)$$

From equation (2);

$$\sigma_s - \sigma_l = \sigma_l \cos \theta = A \quad (3)$$

From equation (3), A can be measured indirectly as the product of liquid surface tension, σ_l and contact angle, θ , when the gravitational effect can be neglected, that is, the drop is very small.

On the other hand, the wetting of a liquid in spreading on a plain surface has been given by Yu.V. Goryunov,³⁾ as shown in eq. (4), furthermore when the meniscus of the liquid drop is assumed as a part of sphere;

$$r = \left(\frac{6}{\pi} m \frac{\Sigma}{K} \right)^{0.25} T^{0.25} \quad (4)$$

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* Professor

** Research Instructor

*** Assistant

**** Graduate Student (at present, Kawasaki Steel Corp.)

where r is radius of the spread liquid drop, and m is mass of the liquid drop, and T is the time of spreading, and K is a constant. Σ is $W_s/\rho\eta$. Where ρ is the difference of densities of liquid metal and liquid flux, and η is the sum of viscosities of those, and W_s is the spreading wetting, which is given generally by following equation;

$$W_s = \sigma_s - \sigma_i - \sigma_l = A - \sigma_l \quad (5)$$

In equation (4), m and T are given by experimental conditions and ρ and η can be measured directly by other methods, or are given from a certain literature. Accordingly, when $K=1$ is assumed, the relative value of the wetting, W_s can be calculated reversively by substituting the measured radius for the term of r of eq. (4).

The wetting of a liquid rised in a vertical capillary joint which consists of infinite parallel two plates can be calculated simply from equation (6);

$$H = \frac{2\sigma'_i \cos \theta}{(\rho_1 - \rho_2) g \cdot r} \quad (6)$$

where H is the equilibrium rising height of liquid, and ρ_1 is the density of liquid metal and ρ_2 is the density of, for example, flux, and r is the distance between two plates. σ'_i is the interfacial surface tension at liquid-flux interface, and the product of σ'_i and $\cos\theta$ expresses the wetting, A , in this case, of course, although the product is introduced by applying the Laplace equation on surface tension at a lowest part of meniscus formed in the capillary gap. In above equation, r is given by experimental condition and ρ_1 and ρ_2 are given from a certain literature and g equals 980 cm/sec^2 . Accordingly, the absolute value of the wetting, A can be calculated reversively by substituting the measured equilibrium rising height of liquid for the term of H of eq. (6).

The wetting of a liquid penetrated in a horizontal capillary joint which consists of infinite parallel two plates can be calculated from the effective penetration coefficient given by A. Latin;

$$k_f = \frac{\sigma'_i \cos \theta}{2(\eta_1 + \eta_2)} \quad (7)$$

where k_f is the effective penetration coefficient, and η_1 is the viscosity of liquid metal and η_2 is the viscosity of, for example, flux. In above equation, the denominator expresses the wetting. Accordingly, when k_f is given by a experiment, the calculation of the absolute wetting, A is possible by the method which mentioned above already.

3. Experimental devices and procedures

3.1 Area-of-spread tests

Two tests, which are in air and in a vacuum, were made. The base plate specimen used in air was pure copper, its size $40 \times 40 \times 0.5 \text{ mm}$, and before test it was polished with emery paper No. 6 and degreased, and the whole surface was fluxed enough with saturated ZnCl_2 aqueous solution or water white rosin. The Pb-Sn alloys of required composition which used in the experiments were prepared by alloying together pure tin and pure lead in a crucible, using a plain rosin as flux, and after solidfy they were cut into a pellet of 3.7 mm^3 every compositions. Tests were made by placing the base plate specimen horizontally on a stainless steel plate (c.f. horizontal plate of Fig.2) heated to a desired test temperature, and the pellet of the solder of required composition was positioned previously in the center of the base plate specimen. Heating time was 2min. and the specimen reached to the desired test temperature in about a half of the time. Accordingly, the holding time is approximately 1 min., while the enhanced spreading was kept constantly. In the test was made in a vacuum, the kind of the specimens used was pure copper and pure nickel without fluxes. The specimen was inserted horizontally to a retort evacuated to about $5 \times 10^{-5} \text{ mmHg}$ and the procedure was same as the case of in air, but the holding time of the specimen in the retort was from 20 - 40min. as shown in Fig. 1. Fig. 1 shows, as one example, the relation between the spread area of Sn on copper specimen at 330°C under $5 \times 10^{-5} \text{ mmHg}$ and the holding time, and zero of the holding time, as shown in the appendix figure, means the time when the specimen temperature reached to 330°C . In Fig. 1, the area increases gradually till 20min., but for over the time the area saturates. It was considered, therefore, that the

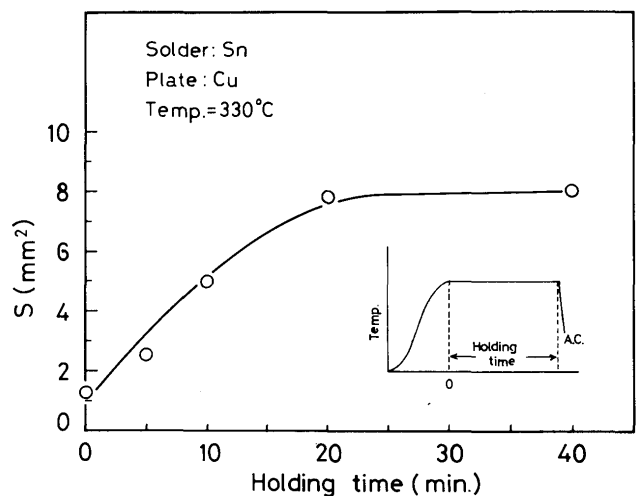


Fig. 1 Spreading rate curve of Sn solder on copper in vacuum

equilibrium relation between the specimen temperature and the atmosphere temperature in the retort was not obtained in the increasing range of the area, because of the small size of the specimen for the retort volume. Then, the holding time was chosen as mentioned above in the vacuum test. Furthermore, in this experiment, it should be noted that all the area of the observed drop belonged to a primary spreading. The spread area was measured with a planimeter.

3.2 Vertical penetration tests

The used joint specimen consists of a pair of copper plates, 22x120x1mm, prefluxed with saturated ZnCl₂ aqueous solution on the innersurface of the plates, and placed the steel spacer of 0.1mm thickness and 2mm width to maintain a capillary gap, and the whole specimen was bound with Mo wire of 0.25mmφ.

Then, the specimen, as shown in Fig. 2, was dipped

above the surface of bath, middle and top parts of the specimen, respectively. In the figure, the curve of "Dip into bath" is the result when the specimen was preheated for 6min. in the furnace, and in this case the time holding in the bath is about a half that of the non-preheated specimen.

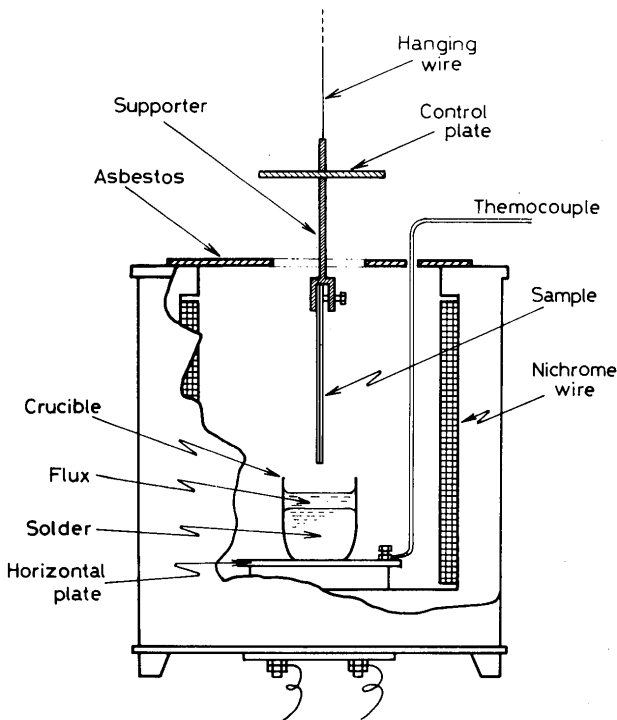


Fig. 2 Apparatus for capillary penetration test

vertically in a crucible, which contains a constant volume of the solders heated to a desired test temperature. The dipping time was 14min. when the specimen was not preheated and it was 8min. when the specimen was preheated, suspending for 6min. in the furnace as shown in Fig. 2. The whole specimen reached enough to the desired test temperature during these times, as shown in Fig. 3 as one example, which shows the temperature rising curves when the specimen was dipped in the molten pure tin of 330°C. The measurements of temperature of specimen in this case were made at ④, ⑤ and ⑥, the positions of those are just

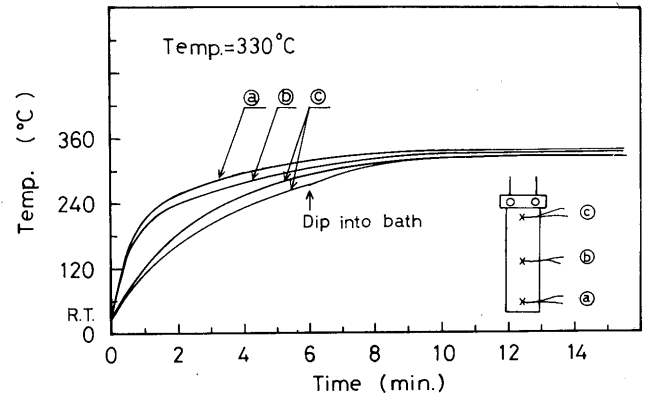


Fig. 3 Temperature rising curves of test pieces dipped in solder bath

4. Results and discussions

4.1 Wetting in spreading on plane surface

The area-of-spread tests were made, at first, to know the effect of fluxes, which are ZnCl₂ saturation aqueous solution and water white rosin, on the spreading of solders of required compositions. The result is shown in Fig. 4. Test temperature was 100°C of

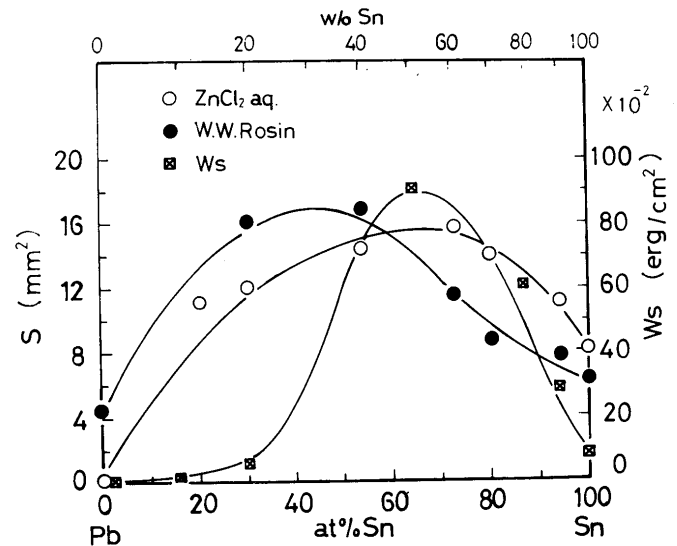


Fig. 4 Spreading and wetting of Pb-Sn solders on copper with saturated ZnCl₂ aq. soln. at 100°C of superheat, and spreading of the solders on copper with water white rosin at just above the liquidus of solders

superheat above the liquidus of used solders for ZnCl₂ flux and just above the liquidus of one for water white rosin in order to prevent the carborization of abietic

acid of main component in the rosin. From this result, it was recognized that, as is well known generally, the shape of the spreading curve of solders on copper plates was mountainous. The composition that shows the maximum spreading, however, depends on a kind of flux used. Then, the second experiment was made at same temperature conditions in a vacuum, and the result is shown in Fig. 5. The spreading curves in a vacuum also

maximum spreading that obtained in using of $ZnCl_2$ flux approximately agrees with the result that made for copper plate in a vacuum. Then, the third experiment was made to know the effect of test temperature on the spreading of solders, and the result is shown in Fig. 6. In this case, moreover, the temperature conditions differ from the first and second experiments mentioned above, that is, it is constant for each solder. In Fig.6, it is evident that the composition of the maximum spreading shifts to a lower tin side as the temperature decreases. From the fact, it is presumed that the result of rosin in Fig. 4, that is a lower tin side, showing the effect of the test temperature. As mentioned already, the temperature for rosin flux is less $100^\circ C$ than that for $ZnCl_2$ saturation aqueous solution flux.

The results obtained from these experiments, anyhow, showed that the spreading curve of Pb-Sn solder on copper plate has a maximum at the intermediate range of composition and is mountainous. Then, to consider the wetting between the solders and copper plate, the relation between W_s of eq. (4) and the composition of solder was calculated by substituting the spread area measured with $ZnCl_2$ saturation aqueous solution flux in Fig. 4 for the term of r of eq. (4), of course, the area was converted into the radius. In this calculation, other factors such as m , K and T were utilized as a constant = 1, and the values shown in Table 1 were used for ρ and η . Table 1 shows the physical properties of Pb-Sn solders and $ZnCl_2$ melted at $100^\circ C$ of superheat just above the liquidus of its solders, and these values were obtained from some references. Here, a suffix 1 shows the solder and 2 means $ZnCl_2$ used as flux.

Now, the marks, “ \boxtimes ” in Fig. 4 are the calculation results and the same marks in Fig. 5 also are the results that calculated by the same means, using the measured values of the spreading of solders on copper plate. But, in the latter, η_2 and ρ_2 were neglected because of the experimental results in a vacuum. As can be seen in both figures, the exponent of value of W_s in Fig. 4 is greater one order than that of W_s in Fig. 5. This appears to due to the assumption condition of m , K and T in the calculation. From this data, anyhow, it should be noted that the shape of wetting curve is similar to one of spreading curve and they are a mountainous type. That is to say, the optimum combination of spreading and wetting properties yields evidently with solders of the intermediate range of composition.

4.2 Penetration tests

4.2.1 Wetting in vertical capillary penetration

The equilibrium rising height of solders risen in the

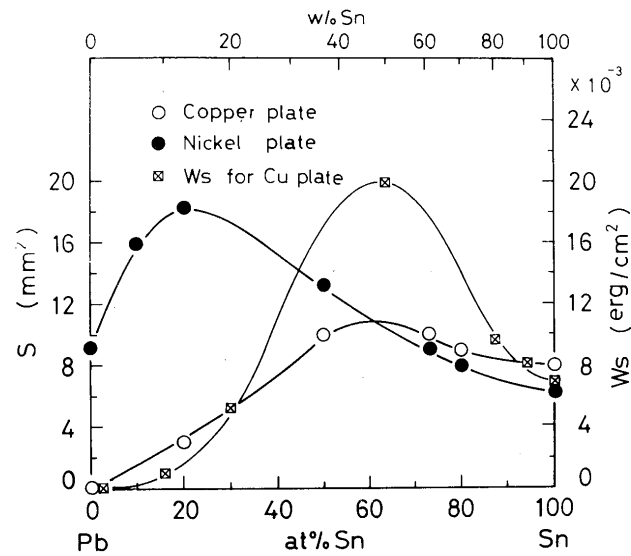


Fig. 5 Spreading and wetting of Pb-Sn solders on copper and spreading of the solders on nickel with no flux at $100^\circ C$ of superheat in vacuum

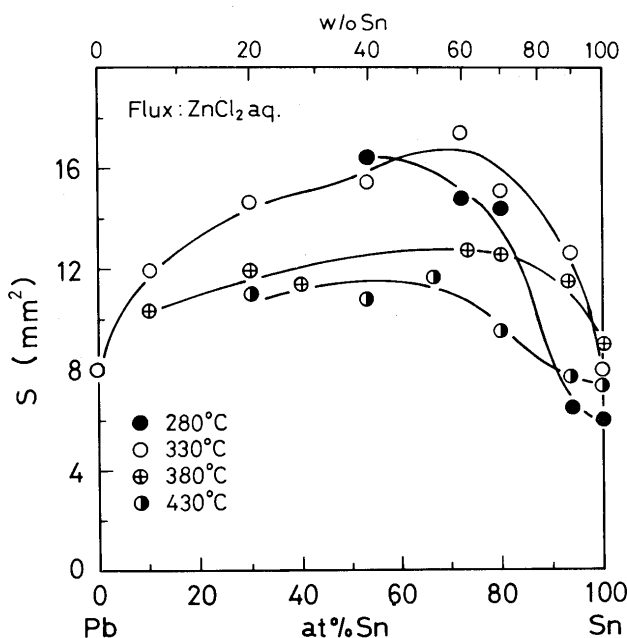


Fig. 6 Spreading of Pb-Sn solders on copper with saturated $ZnCl_2$ aq. soln. at various temperatures

are much the same, except that the position of the maximum spreading depends on a kind of base metal used. But, it is an interest that the position of the

Table 1 Various physical properties of molten Pb-Sn solders and ZnCl₂, and wetting calculated from penetration coefficient in A. Latin's data

(w%)	Sn	90Sn	80Sn	50Sn	20Sn	10Sn	Pb	Ref.
Liquidus + 100°C	332	318	303	310	380	402	427	
σ_i' dyne/cm	543	475	463	446	400	375	311	MIMA ⁴⁾
ρ_1 g/cm ³	6.89	7.17	7.43	8.39	9.80	10.05	10.54	GEBHARDT ⁵⁾
ρ_2 g/cm ³	2.52	2.54	2.55	2.54	2.50	2.48	2.47	H.B. ⁶⁾
η_1 cP	1.56	1.73	1.86	2.22	2.20	2.21	2.22	GEBHARDT
η_2 cP	25	47	73	60	4.8	3.5	3.5	H.B.
k_f (cm/s) x 10 ⁻³	9.3	7.5	6.4	5.3	4.4	5.1	5.1	by LATIN
A (dyne/cm) x 10 ⁻¹	494	731	960	660	62	58	58	in H.P.

capillary copper joints, of which the test method was mentioned in 3.2, at 100°C of superheat just above the liquidus of each solder is shown in Fig. 7 (mark "●"). The actual results showed, as is well known generally, the maximum equilibrium rising height at pure tin. In Fig. 7, the curve of mark "○" means the "Ideal wetting" rising height that calculated by assuming $\cos\theta = 1$ in eq. (6), substituting the values shown in Table 1 for σ_i' (= interfacial tension at molten solders-molten ZnCl₂ interface). In this calculation, the values of Table 1 were used for ρ_1 and ρ_2 , and 980 cm/sec² for g and 0.01 cm for r. It is well known that the curve of the "Ideal wetting" rising height is similar to the curve of actual rising height, which is controlled by the capillary constant of the product of the "Ideal wetting" rising height and the gap distance between plates, r.

But, this view point appears to mistake because of the thermodynamic theory that the immersional wetting, W_i is unrelated to the surface tension of liquid to be used, as shown in following eq. (8), corresponding to

eq. (5);

$$W_i = \sigma_s - \sigma_l = \sigma_l \cos \theta = A \quad (8)$$

In above equation, it is a mistake to assume $\cos\theta = 1$ ($\theta = 0^\circ$), because the immersional wetting varies in proportion to the surface tension of liquid, σ_l . Then, $\sigma_l' \cos\theta$ (=A) of eq. (6) was calculated inversely by substituting the actual rising height for H. The marks "△" in Fig. 7 are the results. The shape of this curve also is mountainous and similar to the wetting curves of Figs. 4 and 5.

Compared with the immersional wetting (Fig. 7) and the spreading wetting (Figs. 4 and 5), however, it should be noted that the difference of the wetting at near eutectic composition and at pure tin is smaller in the case of the immersional wetting than the spreading wetting. As the reason of this, the energy difference between the immersional wetting and the spreading wetting was considered, as shown in Fig. 8. And also, as shown in eqs. (5) and (8), the difference in both wetting is given by the surface tension of liquid, then in Fig. 8, the addition of the surface tension of solders to the

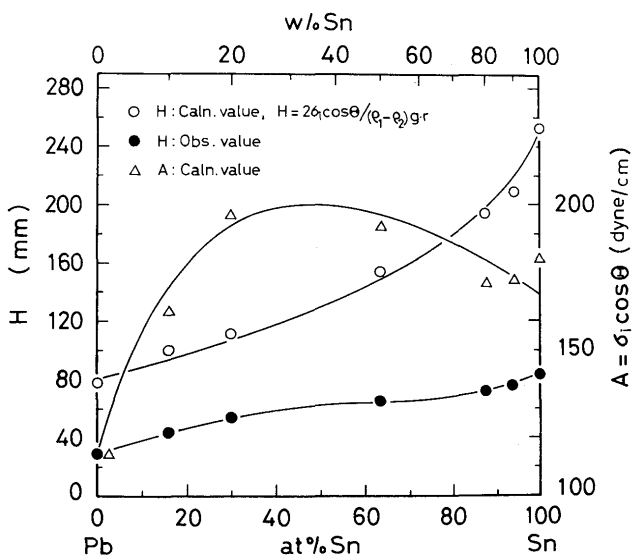


Fig. 7 Equilibrium and ideal rising height, and wetting of Pb-Sn solders in vertical capillary copper joints with saturated ZnCl₂ aq. soln. at 100°C of superheat

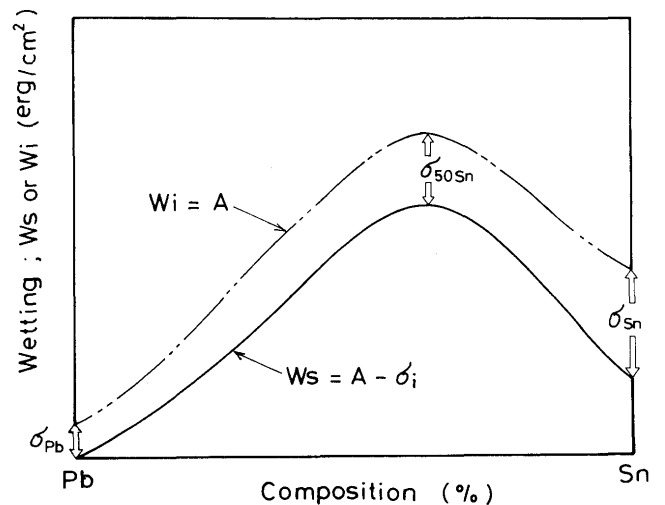


Fig. 8 Schematic illustration of both energy terms of spreading wetting and immersional wetting

spreading wetting, W_s yields the immersional wetting, W_i . Here, as shown in Table 1, the interfacial tension at pure tin-ZnCl₂ interface is greater than that at 50wt% tin alloy-ZnCl₂ interface, accordingly, the difference of the immersional wetting at near eutectic composition and at pure tin becomes narrower obviously.

From this consideration, it is evident that the discrepancy in both phenomena of spreading and capillary-penetration tests, which were mentioned

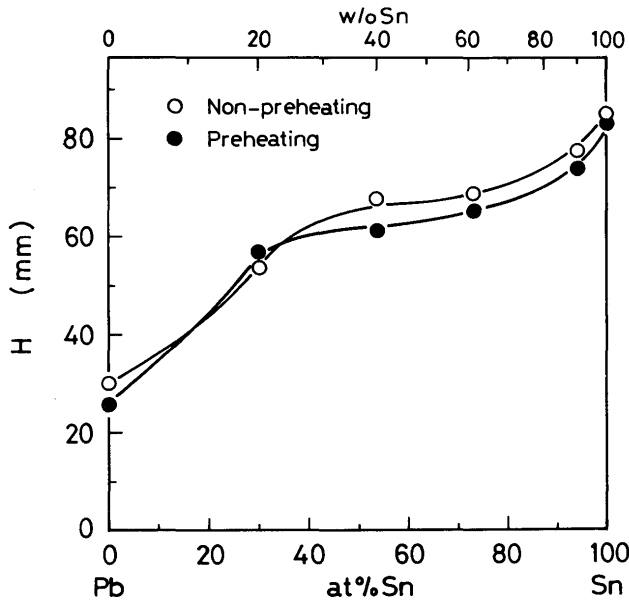


Fig. 9 Equilibrium rising height of Pb-Sn solders in vertical capillary copper joints with and without preheating

already in "Introduction", is attributed to the fact that the interfacial tension of pure tin is greater than that of the solder containing about 50wt% of tin. Here, the flow of liquid can be neglect on this consideration, because it is included in the "A" of eqs. (5) and (8), accordingly, it is a common factor on the comparison of both the wetting.

Figure 9 shows the result of experiment made to know the effect of the contamination of solder bath containing copper base plates on the penetration height of solders, varying the immersion time of base plates with the procedures of non-preheating and preheating, as mentioned already in 3.2. The contamination occurs by the dissolution of base plates into the original solder

bath, accordingly, the rising height of solder may be effect by the variation of the composition of the solder bath. As can be seen in the result, but, the height in both is similar to in the range of this experiment. Table 2 shows the thickness of alloy layer formed at interface between the solidified solders and copper plate. The measurements were made in the case of eutectic solder and pure tin bathes and at both positions of the bottom, (a) and top, (c) sides of specimen with EPMA. In the concentration curve obtained, the diffusion layer of copper element was judged by applying the relation of $3\sqrt{Dt}$. There is not the considerable difference, or is the difference to be neglect as experimental errors in both preheating and non-preheating. On the other hand, other researchers⁷⁾⁸⁾ have reported the time that the solders reach to the equilibrium rising height after the specimens were dipped in the solder bath. According to their results, it is within several seconds, although it is 8 to 16 minutes in our experience as shown in Fig. 3. Accordingly, from these results, it will be justified that the effect of contamination in a penetration test can be neglected generally.

4.2.2 Wetting in horizontal capillary penetration

Figure 10 shows the result of Latin, who found

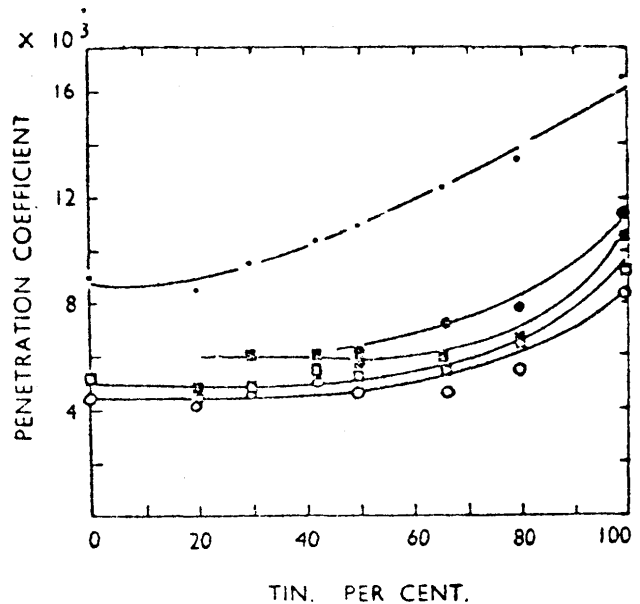


Fig. 10 Penetration coefficient of Pb-Sn solders in horizontal capillary copper joints at various degrees of superheat by A. Latin

Table 2 Thickness of copper diffusion layer formed at interface between copper plate and Sn or Pb-Sn eutectic solder

Preheating				Non-preheating			
62wt%Sn-Pb		Sn		62wt%Sn-Pb		Sn	
Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top
11.6μ	10.8μ	12.6μ	7.2μ	9.6μ	5.4μ	10.4μ	10.0μ

that, between copper surfaces, the highest effective penetration coefficient was obtained when the liquid metal was pure tin. From this data, we calculated the wetting that is given by $\sigma'_1 \cos \theta$ of eq. (7), using the values of penetration coefficient of 100°C superheat in Fig. 10. Those used values are shown in the column above the last column of Table 1, and the last column is the calculation values of the wetting. In the table, the maximum value of wetting is obtained at about 80wt% Sn of the solders and the tendency of wetting is mountainous. The order of calculated values, however, is large than that of wetting values obtained in Figs. 4, 5 and 7. As the reason, it is presumed that although the viscosity of "NH₄Cl + D.T.D. 81 + 0.1% Teepol X", which is the flux in Latin's experiments, must be used for η_2 of eq. (7) in this calculation, the viscosity of molten ZnCl₂ is used conveniently because of unknown details on the flux. Accordingly, they are not absolute values, but relative values. This result and from the results of Figs. 4, 5 and 7, anyhow, it is evident that the tendency of wetting between Pb-Sn solders and copper is mountainous and the maximum wetting occurs with the solders of the intermediate range of composition.

5. Conclusions

This investigation was made to clear the course of the discrepancy in both spreading and penetration of Pb-Sn solders in contact with copper plates. The discrepancy that is well known, at first, was confirmed by experiments and the obtained results were considered from a view point of thermodynamic wetting at liquid-solid interface.

These results are summarized as follows;

- 1) The maximum wetting between the solders and copper is obtained at the intermediate (near eutectic) composition of solders, and the shape of wetting curve is mountainous in both tests of the spreading and the penetration. The solder of eutectic composition, accordingly, has both properties of a good wetting and spreading.
- 2) The discrepancy in both tests of the spreading and the penetration can be attributed to the fact that the surface (or interfacial) tension of pure tin is greater than that of the solder of the intermediate composition.
- 3) The flow of solder in contact with copper solid surface is controlled by factors such as the wetting between the solder and copper, the density and viscosity of solder and flux used. A good flowing, therefore, is not always a good wetting and the converse holds good.
- 4) In the calculation of immersional wetting, it is a mistake to taking the "Ideal" wetting condition into account.

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