Title	The Study on Spreadability of Solder on 18-8 Stainless Steel Plate
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Editor(s)	
Citation	Bulletin of University of Osaka Prefecture. Series A, Engineering and natural sciences. 1972, 21(1), p.163-173
Issue Date	1972-09-30
URL	http://hdl.handle.net/10466/8204
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The Study on Spreadability of Solder on 18–8 Stainless Steel Plate

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(Received June 15, 1972)

In this report, authors have discussed about spreadability of solders on 18–8 stainless steel (SUS27) plate. The results obtained from this investigation are as follows.

(1) Spread area of solders on SUS27 plate with $ZnCl_2$ system anhydrous molten salt fluxes is increased when NH_4Cl is contained in fluxes.

(2) Spread area of Sn–Pb eutectic solder on SUS27 plate with $ZnCl_2$-NH_4Cl-$SnCl_2$ fluxes contained a large quantity of both NH_4Cl and $SnCl_2$ is remarkably large.

(3) Spread area of Sn–Pb eutectic solder on SUS27 plate with Rosin-$C_6H_5NH_2 \cdot HCl$ is comparatively large.

(4) In due consideration of various phenomena, wettability of Sn–Pb eutectic solder on SUS27 plate is not always correctly decided by spreading test.

(5) If previous treatment of soldering on SUS27 plate is carried out, a pickling solution mixed H_2SO_4 with HNO_3 makes a slight increase in spread area.

1. Introduction

Spreadability of solders is affected by the mutual action between the base metal and the solder. Namely, spreadability of solders is varied by the chemical composition of solders even in the same base metal and flux. And in this case, spreadability of solder is little affected by the interfacical tension (γ_L) between solder and flux. Accordingly, to get an excellent spreadability, the metallic contact between a base metal and a solder is necessary. Spreadability of solders is remarkably lowered by prevention of the mctallic contact between solder and base metal when the oxide film exists on base metals. And then the oxide film on base metal results in a cause for lowering of the surface tension (γ_S) of the base metal.** [1),2)]

As shown in the following formula, the lowering of this γ_S results in the lowering of spreadability though lowering of γ_S is the secondary factor.

$$\gamma_L \cos\theta = \gamma_S - \gamma_{S/L} \qquad \text{where } \theta\text{: contact angle.}$$

In this view, an elimination of the oxide film on base metal is very important to get an excellent spreadability of solder. Soldering of 18–8 stainless steel is generally difficult in comparision with mild steel, copper and brass. As one of various causes, it is considered that the heat conductivity of 18–8 stainless steel is smaller than that of mild steel or copper and its heat expansion coefficient is larger. And as the cohered oxide film exists on stainless

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** When the metallic contact between a base metal and a solder is perfectly obstructed, the molten solder can not spread on base metal as it is globular shape. In this case, the value of interfacial tension ($\gamma_{S/L}$) between solder and base metal is comparatively large. On the otherhand, in the case of metal-metal contact, it is not large. And spreadability of solder is governed by the value of $\gamma_{S/L}$ in many cases.[2)] steel base metal, soldering of 18-8 stainless steel is more difficult. Elimination of above oxide film by flux is comparatively difficult as a fair chance for re-oxidation of base metal is occured even when a tarnish film is eliminated just before soldering.

In this report, the spreadability of solder on the 18-8 stainless steel with various fluxes have been discussed. Up to now, $ZnCl_2$-NH_4Cl-$SnCl_2$ system flux have been used for soft soldering of such a kind of metal.[3] From our experimental result, an addition of costly $SnCl_2$ is not always necessary for the improvement of spreadability. If a tinning action by $SnCl_2$ contributes to protection of re-oxidation, this action can be compensated by the other method.

2. Experimental Procedures

Experimental equipment and procedures are illustrated in the previous report.[4]

Base metal: SUS27 plate (40×40×0.6 m/m). In this test, grease and dust on base metal as recieved were removed with acetone just before testing.

3. Results and Discussions

3.1. Spread area of Sn-Pb eutectic solder with $ZnCl_2$ system flux on SUS27 plate

Fig. 1 shows the spreadability of Sn-Pb eutectic solder with $ZnCl_2$ base fluxes on SUS27 plate. And in all cases, spread area of Sn-Pb eutectic solder is increased with the secondary component chlorides (NH_4Cl or $SnCl_2$). Spread area of Sn-Pb eutectic solder is

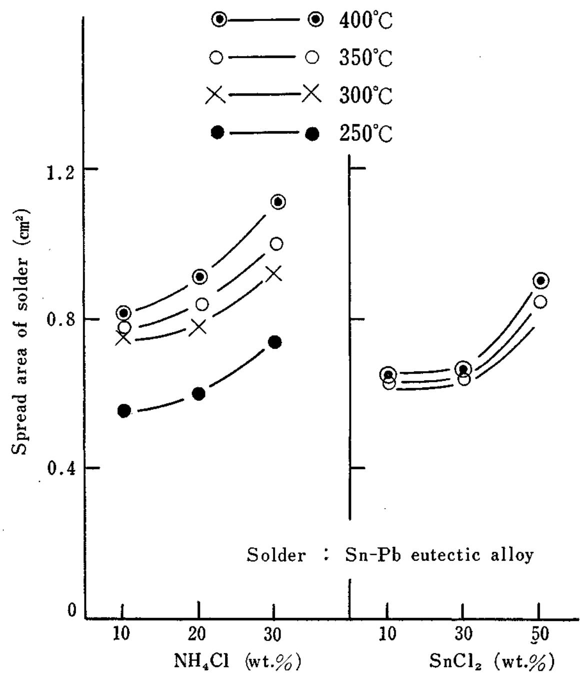

Fig. 1. Spread area of Sn-Pb eutectic solder with $ZnCl_2$-NH_4Cl and $ZnCl_2$-$SnCl_2$ binary fluxes on SUS 27 plate.

remarkably increased in 50 Wt % $ZnCl_2$–50 Wt % $SnCl_2$ flux. This increase of spread area may be due to alloying action between solder and Sn produced by the substitutional precipitation of $SnCl_2$ at the spreading edge of solder. As shown in Fig. 2, these phenomna arise even on SPCl plate. When the more quantity of $SnCl_2 \cdot 2H_2O$ is contained, the perfect elimination of H_2O in fluxes is difficult. And in the combination of both SUS27 base metal and $ZnCl_2$–$SnCl_2$ fluxes, this H_2O may give the effect on spread area of solders. In the combination of SUS27 base metal and $ZnCl_2$–NH_4Cl fluxes, HCl produced by heat decomposition of NH_4Cl activates above fluxes and gives a comparatively good spreadability of solder at about 300°C over. Nevertheless, spreadability of solders at 250°C is inferior to 300°C as heat decomposition of NH_4Cl at 250°C doesn't active.

Solders with $ZnCl_2$, $ZnCl_2$–KCl, $ZnCl_2$–NaCl and $ZnCl_2$–KCl–NaCl fluxes don't spread on base metal surface and the shape of solder is kept on a globular. If a solder is placed on a base metal when flux is just melted and slightly vasicating, a molten solder of globular shape is spreaded violently on a base metal by pushing a circumferential flux. In this case, the re-oxidation of base metal is not comparatively progressed as flux is just after melting and the eliminating ability for oxide film by flux is given by H_2O remained in the molten salt flux.

Spread area of Sn–Pb eutectic solder with pure $ZnCl_2$ flux on SPCl base metal is very large, but it decreases into comparatively small in the case of $ZnCl_2$–$SnCl_2$ system flux. And lowering of this spreadability isn't recovered even when $ZnCl_2$–$SnCl_2$–NH_4Cl system flux added NH_4Cl which have the large eliminating ability for oxide film is used.

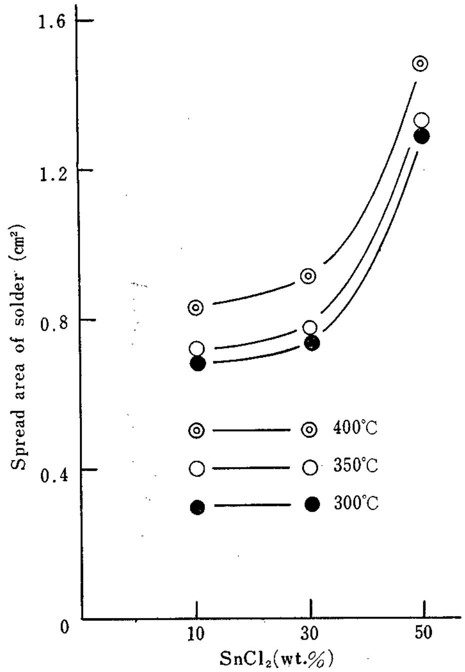

Fig. 2. Spread area of Sn–Pb eutectic solder on SPCl plate with $ZnCl_2$–$SnCl_2$ binary fluxes.

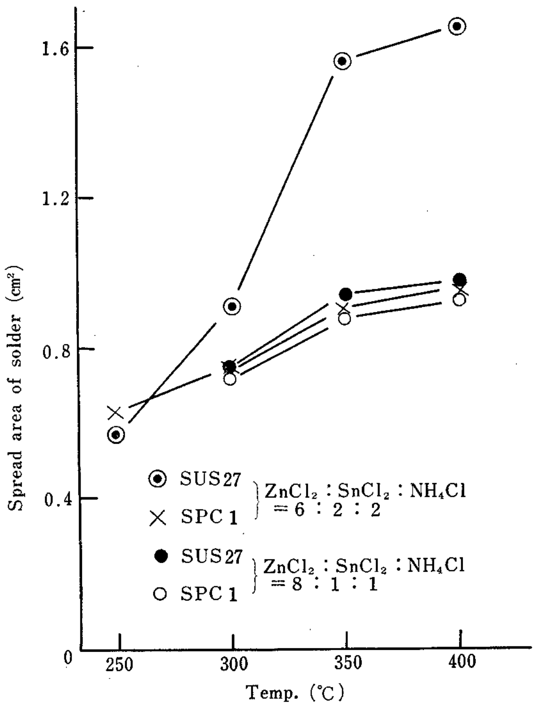

Fig. 3. Spread area of Sn–Pb eutectic solder with $ZnCl_2$–$SnCl_2$–NH_4Cl ternary fluxes on SUS 27 and SPCl plates.

Fig. 3. shows the spreadability of Sn-Pb eutectic solder with $ZnCl_2$-$SnCl_2$-NH_4Cl system flux on SUS27 or SPCl base metal. As ascertained from Fig. 3, spread area of solder with flux containing a large quantity of $SnCl_2$ and NH_4Cl on SUS27 increases remarkably. But spreadability of solder with above fluxes on SPCl base metal doesn't arise such phenomena.

Fig. 4 shows the spread area of Sn-Pb eutectic solder with ternary fluxes which don't contain $SnCl_2$ on SUS27 base metal. In this case, though the spread area of solder is increased when the added quantity of NH_4Cl is increased, the increase of spread area isn't specially remarkable. Fig. 5 shows the spread area of solder with quarternary system fluxes on SUS27 base metal. And spread area of this solder isn't remarkably increased as added quantity of $SnCl_2$ and NH_4Cl to $ZnCl_2$ is very little. As shown in Fig. 6, Sn-Pb eutectic solder on SUS27 base metal spreads larger in proportion to the increment of $SnCl_2$ and NH_4Cl to $ZnCl_2$. But the spread area of Sn-Pb eutectic solder on SPCl base metal

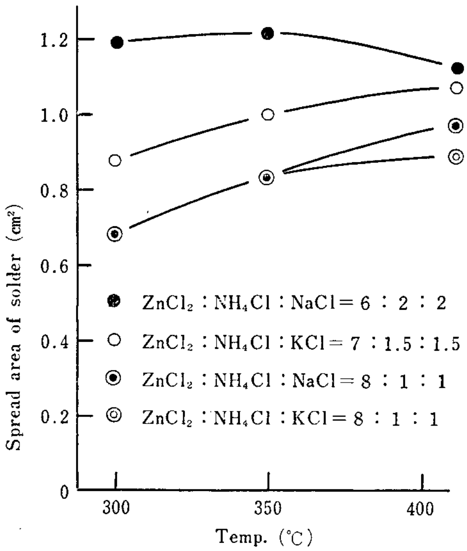

Fig. 4. Spread area of Sn-Pb eutectic solder with ternary system flux which don't contain $SnCl_2$ on SUS27 plate.

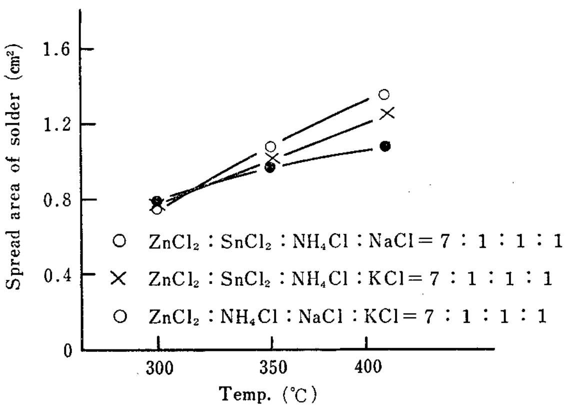

Fig. 5. Spread area of Sn-Pb eutectic solder with various quarternary system fluxes on SUS27.

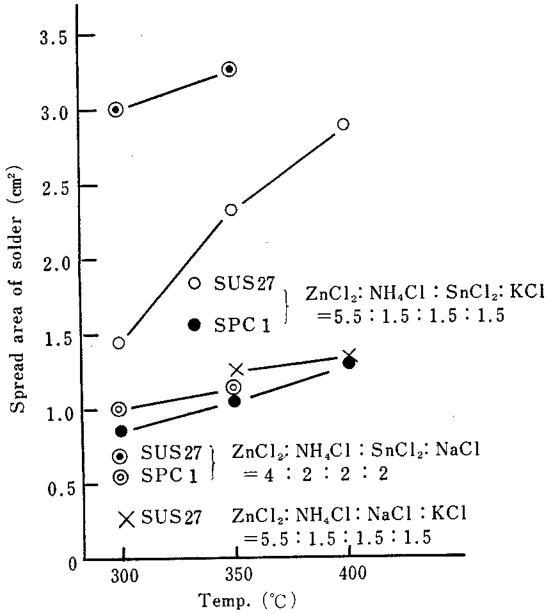

Fig. 6. Spread area of Sn–Pb eutectic solder with quarternary fluxes on SUS27 and SPCl plates.

doesn't turn into excessively large in spite of the increment of $SnCl_2$ and NH_4Cl to $ZnCl_2$. And the spread area of Sn–Pb eutectic solder on SUS27 base metal isn't increased when $SnCl_2$ isn't added in $ZnCl_2$-NH_4Cl_2 systsm flux. In short of the above experimental result, the spread area of Sn–Pb eutectic solder is remarkably large if the following both conditions are satisfied.

(1) SUS27 is used as the base metal.

(2) Flux contains a large quantity of both $SnCl_2$ and NH_4Cl.

And this phenmenon is promoted by adding KCl, NaCl or KCl–NaCl to $ZnCl_2$–NH_4Cl–$SnCl_2$ fluxes. But, when one factor in following conditions is satisfied, spreadability of solder doesn't improve remarkably.

(1) SPCl is used as the base metal.

(2) NH_4Cl or $SnCl_2$ isn't contained in flux.

(3) The quantity of $SnCl_2$ and NH_4Cl is very little.

Accordingly. the causes of remarkable spreading phenomena of Sn–Pb solder are considered as follows.

(1) A large quantity of gas is produced by decomposition of NH_4Cl at high temperature when a large quantity of NH_4Cl is contained in flux.

(2) If a quantity of NH_4Cl is increased, Cr composions produced by attack of flux to SUS27 base metal are increased as the activity of flux increases.

(3) $ZnCl_2$–$SnCl_2$–NH_4Cl system flux containing large quantity of Cr compositions becomes very viscous.

Accordingly, the comparativily large bubbles are produced and then disappeared. This action of bubbles makes a molten solder shake and then a spread area of solder is increased by this action of bubbles.

On SPCl base metal, flux doesn't turn into viscosity as Cr compsitions are not contained in flux and from this reason, spread area of this solder isn't increased almostly. As shown in Fig. 7, a spread area of Sn–Pb eutectic solder on SUS27 base metal with Rosin–$C_6H_5NH_2 \cdot HCl$ flux become turns into very large. $C_6H_5NH_2 \cdot HCl$ has an elimination ability for oxide by evolution of HCl at high temperature when Rosin–$C_6H_5NH_2 \cdot HCl$ system flux is used. And in this case, flux vesicates severly and it is considered that this vesication may give an effect to spreadability of solder. On the otherhand, when H_3PO_4 is used as flux, a spread area of Sn–Pb eutectic solder on SUS27 becomes comparatively large, but this solder on SPCl is not spreaded entirely. H_3PO_4 is very active to SPCl, so that this flux becomes inferior in quality by the strong reaction between flux and base metel on the way of heating. Therefore, the function of flux is lossed at spreading temperature range of solder. HCl is volatilized easily by heating and more consumed by reaction with base metal before base metal is heated to spreading temperature range of solder. So that the spread area of solder on both SUS27 and SPCl base metal isn't good. Furthermore, Fig. 7 shows the spread area of solder on Cu and brass base metals in comparision with SUS27 base metal.

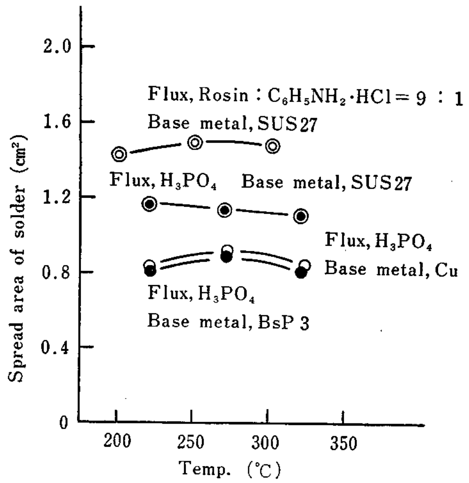

Fig. 7. Spread area of Sn–Pb eutectic solder on various base metals.

Fig. 8 and Fig. 9 show the spread area of various binary solders on SUS27 base metal. Spread area of Pb–Cd solders are comparatively large when above solders are combined with $ZnCl_2$–NH_4Cl system flux. As Cd is an easily oxidizable metal and elimination of this oxide film is not easy, when $ZnCl_2$–$SnCl_2$ system flux which don't contain NH_4Cl having the strong eliminating ability for oxide film is used, above solders are not almost spreaded. Spread area of above solders grows into larger due to Sn prduced by substitutional precipitation of $SnCl_2$ when $ZnCl_2$–$SnCl_2$–NH_4Cl system flux is used. Spread area of Zn–Sn binary solders is small at 350°C, but it grows into larger at 400°C. On Zn–Sn solder, a special reaction between solder, flux and base metal at spreading edge of solder is observed. Spread area of this solder may be small at 350°C as liquidus line of solder is near to 350°C. At 400°C, Zn–Sn solder spreads greatly. And one reason of this phenomenon may be connected with above special reaction which is observed apparently.

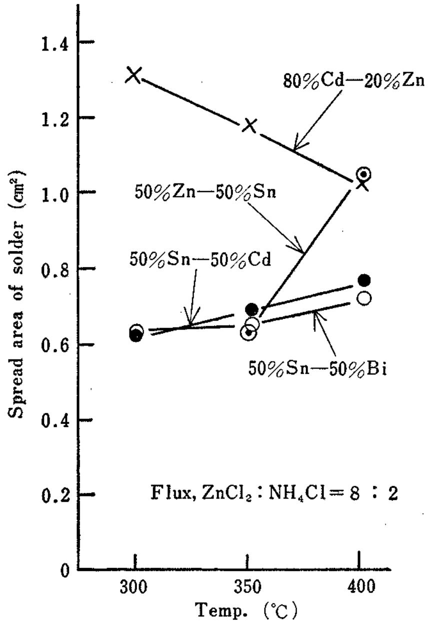

Fig. 8. Spread area of various binary system solders on SUS27 plate.

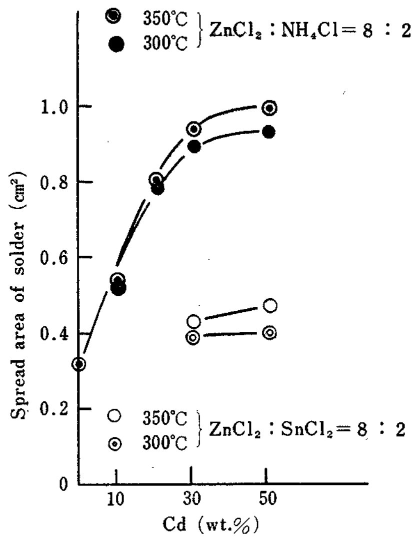

Fig. 9. Spread area of Pb-Cd solders on SUS27 plate.

3.2. Eliminating ability of oxide film for $ZnCl_2$ system flux

In our experiments, when SUS27 base metal is used, oxide film on base metal is eliminated on the way of heating as $ZnCl_2$ system flux is aq. solution. And it is considered that surface of base metal is so far cleaned as make solder overspread.* But as known, molten salt flux doesn't always shut out oxygen perfectly. Oxygen which can pass through flux by diffusion and convection can reach to the surface of SUS27 or solder which is prevented a contact with air by flux.** If the flux has an eliminating ability for oxide film when base metal surface is re-oxided, solder is easily spreaded on SUS27 base metal. When flux is just after melted in the combination of SUS27 and $ZnCl_2$, the solder spreads over pushing the flux on base metal surface covered with molten flux.*** When a solder is placed on base metal covered with flux since it has been melted, a solder in melted flux doesn't spread on base metal surface as molten solder can not contact with base metal. This fact shows that anhydrous molten $ZnCl_2$ has not eliminating power for oxide produced by re-oxidation.**** In conclusion, when $ZnCl_2$-NH_4Cl-$SnCl_2$ system flux is used as aq. solution, contribution of each chlorides is shown as follows.

(1) Though the oxide film on SUS27 base metal surface is eliminated by HCl produced as $ZnCl_2$ exists together with H_2O during heating, molten anhydrous $ZnCl_2$ is power-

* If H_2O is volatilized by heating and aq. chloride solution is concentrated, HCl or H^+ ion is produced and then oxide film on base metal is eliminated. For example, $ZnCl_2$ solution turns into about pH 1 at 70% $ZnCl_2$.[5]

** It is said that this oxygen carries out important part on elimination of oxide film in Al base metal.[6]

*** This fact is caused by H_2O which isn't perfectly eliminated.

**** Oxide film is elminated by molten anhydrous $ZnCl_2$ in SCP1 base metal.

less for elimination of oxide film on base metal surface and acts mainly as solvent which dissolves NH_4Cl or $SnCl_2$.

(2) NH_4Cl is decomposed at above 230°C and HCl produced by this decomposition eliminates re-oxidation film.

(3) Accumulated Sn on base metal is produced by substitutional precipitation from $SnCl_2$. And Sn can protect re-oxidation on SUS27 base metal surface and promotes the spreadability of solder. Its effect isn't remarkable when $SnCl_2$ is added to $ZnCl_2$. More spreadability is obtained by alloying reaction between solder and Sn produced by substitutional precipitation at spreading edge of solder. Nevertheless, pure $SnCl_2$ is powerless flux in eliminating ability for oxide film.

As shown in Fig. 10, when $ZnCl_2$ is added into H_3PO_4 solution, spread area of Sn–Pb solders is remarkably reduced.

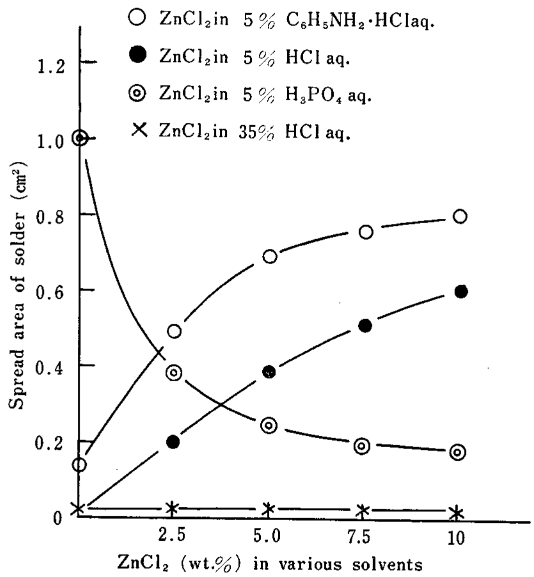

Fig. 10. Effect of $ZnCl_2$ content in various solvents on spreadarea of Sn–Pb eutectic solder at 300°C.

3.3. Relation between pre-treatment of base metal and spread area of Sn-Pb solders

Fig. 11 shows the relation between pre-treatments of SUS27 base metal and spread area of Sn–Pb solders. Spread area may be slightly increased when base metal is dipped in acids polished with #400 emery paper just before spreading test. It is considered that the enlargement of spread area of Sn–Pb solders by the acid treatment is caused by elimination of oxide film and roughness of surface. But, when the flux is used, the effect of elimination of oxide film by acid dipping is comparatively small. And then the effct of roughness may be more remarkable. In disordered unevenness without directional stability, the following Wenzel's law can be applied.

$$\cos\phi = \gamma \cos\theta \qquad \gamma\text{: roughness ratio} \qquad (1)$$

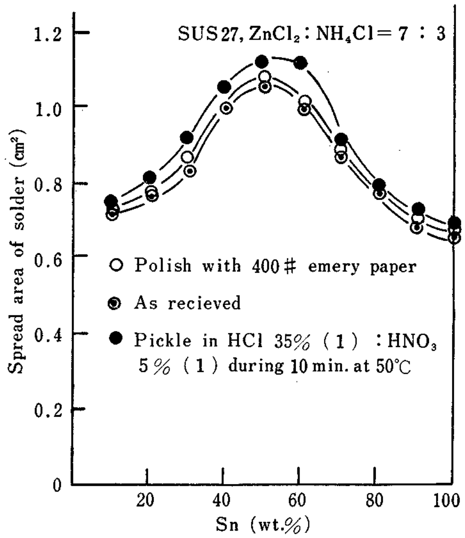

Fig. 11. Effect of surface conditions on the spread area of Sn-Pb solders at 300°C.

In SUS27 and Sn-Pb solders, spreadability of above solders may be promoted as the θ is smaller than $\pi/2$. When a series of scratch line which have directional stability is made with emery paper ($\theta<\pi/2$), spread area of solder is promoted by capillary attraction. But in this case, the Wenzel's law can't apply.

3.4. Spread area of solders by sessile dropping method and height of capillary rise of solders

In Fig. 12, a spread area of ternary solders contained about 2% alloying elements by sessile dropping method is compared with height of capillary rise of same solders on Cu

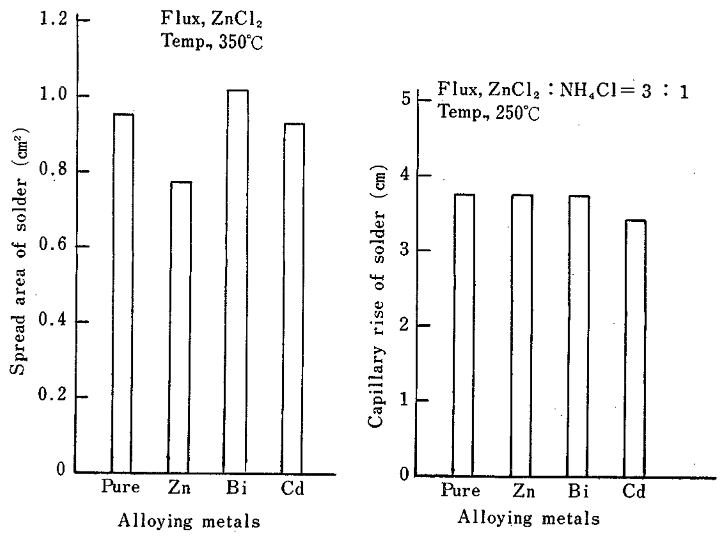

Fig. 12. Relation between the spread area or capillary rise and 2 wt.% other alloying metals added to Sn-Pb eutectic solder.

base metal. Height of solder by capillary attraction (h) is calculated by the following formula.

$$h=\frac{2(\gamma_S-\gamma_{S/L})}{\rho\cdot g\cdot d}=\frac{2\gamma_L\cdot\cos\theta}{\rho\cdot g\cdot d} \tag{2}$$

where g: gravitational acceleration (980.6 cm/sec^2)
ρ: density of solder (g/cm^3)
d: distance of joint gap (cm)
θ: contact angle (degree)

Still more, a relation between contact angle (θ) by sessile dropping method and interfacial tension is shown as follows.

$$\gamma_S=\gamma_L\cdot\cos\theta+\gamma_{S/L} \tag{3}$$

Nevertheless, spreadability of solders isn't always controlled by the formula (3) as stated before. In comparition with $ZnCl_2$ system flux and $ZnCl_2$-NH_4Cl system flux (Base metal: Cu plate, Solder: Sn-Pb eutectic solder), spreadability of solder is remarkably differed even when both γ_L is same value. The spread area of solder is varied extremely at various test temperatures even if the combination of solder, base metal and flux is identical and each of three interfacial tensions changes little. In this case, alloying reaction at the spreading edge of solders may give some effect on spreadability of solders.[7]

Conversely, the height of solders by capillary rise is comparatively controlled by formula (2). For example, when the value of $\gamma_L\cos\theta$ is varied by variation of Sn-Pb solder composition or joint clearance is differed, calculated value by theoretical formula and measured value show a perfect correspondence though the absolute values is differed respectively due to the capillary dum and other causes. Height of solder by capillary attraction (h) and spread area of solder by sessile dropping method (S) show theoretically same tendency so far as interfacial tension (γ_L) between flux and solder isn't varied largely by adding 2% alloying element as induced by formula (2) and (3).

Nevertheles, as shown in Fig. 12, both values are not frequently corresponded as spread area of solder (S) isn't controlled by formula (3). Namely, when Zn, Cd or Bi to Sn-Pb eutectic solder is added, it is considered that Zn or Cd is no effect on interfacial tension (γ_L) of Sn-Pb eutectic solder as interfacial tension (γ_L) of both Zn and Cd is larger than that of Sn-Pb eutectic solder. On the otherhand, though it is considered that interfacial tension (γ_L) of the solder added Bi to Sn-Pb eutectic solder is lowered as interfacial tension of Bi is smaller than that of Sn-Pb eutectic solder, lowering of interfacial tension may be at most 50 dyne/cm. It is doubtful whether spreadability of solder is changed. Namely, even if NaCl is added to $ZnCl_2$, spread area of solder isn't varied though interfacial tension (γ_L) is lowered about 50 dyne/cm. Accordingly, addition of the third compositions (Zn, Cd and Bi) affects on mutual reaction between base metal and solder. And from this view, it may be considered that spreadability of solder is varied by above reasons. Still more, disagreement of relation between spread area (S) and height of capillary rise (h) is observed in the combination of Cu base metal and Sn-Pb solder. The spread area of

Sn–Pb solder shows maximum value at about Sn 50 wt. % but height of capilary rise is maximum at Sn 100 wt. %.

4. Summary

Authors have studied the spreadability of solders on SUS27 base metal. The results obtained are as follows.

(1) On the soldering of SUS27 base metal, $ZnCl_2$, NH_4Cl or $SnCl_2$ is not useful as on independent flux.

(2) In the combination of SUS27 base metal and anhydrous molten $ZnCl_2$ system flux, spread area of Sn–Pb solders is comparatively small when flux doesn't contain NH_4Cl.

(3) Spread area of Sn–Pb solders with Rosin–$C_6H_5NH_2 \cdot HCl$ flux on SUS27 base metal is larger than H_3PO_4 flux.

(4) Spread area of Sn–Pb eutectic solder with anhydrous molten $ZnCl_2$ flux contained a large quantity of both NH_4Cl and $SnCl_2$ is remarkably large.

(5) In the pre-treatments for soldering to SUS27 base metal, pickling with mixed acid by H_2SO_4 and HNO_2 may be more useful than the other pre-treatments.

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