Wettability of Liquid Tin on Solid Copper*

By Ichiro Kawakatsu** and Tadashi Osawa**

For obtaining good joints by soldering, a wettability of liquid metal on the solid metal surface, related to solderability, is one of the most important factors, and the wettability is accelerated by using a suitable flux and atmosphere. In atmosphere soldering the flow of molten solder will be retarded by oxide films on base metals formed by a small amount of oxygen in atmosphere.

In this study a wetting phenomenon of liquid tin on solid copper was clarified in relation to soldering, and the effects of additional elements to pure tin and oxide films on the base metal were mainly examined as the basic factors affecting the wettability. Li, Na and P were selected as additional elements to pure tin for making soldering more efficient. For the wettability test of an oxidized copper base metal, the reaction furnace which keeps the oxygen partial pressure in its atmosphere above the dissociation pressure of Cu_2O was employed to preserve oxide films at the experimental temperature.

It was clarified in this experiment that the activated tin alloys containing Li, Na and P as additional elements showed better wettability, and the effect of P addition was excellent. The spreading area of liquid tin decreases owing to the presence of oxide films, and the spreading area on oxidized copper with Cu_2O (600 Å in thickness) was approximately 50% of that on pure copper at 340°C.

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I. Introduction

The phenomena of wetting and spreading are of prime importance in the formation of brazed and soldered joints. Physical and chemical principles lead to equations governing the shape of liquid surfaces and the rate of filling a capillary gap in the non-interacting systems. For the extension of theory to practical systems, however, special consideration should be given to many complicating factors. In this regard, the removal of oxides is essential, which can be attained by a reducing atmosphere, heating in vacuum or fluxing. Alloying between the filler metal and the base metal is also an important interaction, because it radically affects joint filling in a way of altering the surface tension, viscosity and melting point of the filler metal.

The phenomena of wetting have been studied by many investigators from the standpoints of surface energy, interactions between the filler metal and base metal, viscosity, flux application and so on^{(1)~(5)}. Most of these studies are concerned with wettability of pure metal and alloy, and there are few reports dealing with the effects of oxide films and alloy elements on wettability.

In furnace soldering in a protective atmosphere the wettability of molten solder on a base metal is one of the most important factors and can be interfered by oxide films formed by a small amount of oxygen in atmosphere⁽⁶⁾. Comprehensive reports on furnace soldering in protective atmosphere, however, are few in number. In this study a basic investigation on furnace soldering has been carried out to study the

wettability of liquid tin and activated tin alloys, containing a small amount of Li, Na and P, on copper-base alloys coated with uniform oxide films. Some influences upon the wettability were also discussed.

II. Experimental Procedure

Wettability of molten solder, which is a most important factor in soldering, brazing, hot-dip coating and so on, has been investigated by measurements of spreading, contact angle and capillary action⁽⁷⁾⁽⁸⁾. In this experiment the wettability was investigated in terms of the spreading of liquid tin on the base metal, that is, the spreading area of liquid drop was measured under various experimental conditions.

The specimens used were prepared from cold-rolled copper plates (25 mm × 25 mm × 0.3 mm) with 99.9% purity as the base metal and the punched disks from the as-cast tin plates (4 mm in diameter, 1 mm in thickness) for soldering. The spreading test of liquid tin on solid copper was made by heating the tin disk on solid copper in the furnace for a given time, and the spreading area was measured. An example of the spreading test specimens is shown in Photo. 1.

In this experiment the following two factors were mainly examined as the essential factors affecting the wettability of liquid tin on solid copper.

- (1) Effects of additional elements to pure tin.
- (2) Effects of oxide films on copper plates.

For the investigation of (1), additions of Li, Na and P to pure tin were considered to have influence on the wettability, accompanying the changes in surface tension and chemical property⁽⁹⁾. Sn-0.2%Na, Sn-0.2%Li and Sn-0.2%P alloys were prepared as the

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** Department of Mechanical Engineering, Faculty of Science and Technology, Aoyamagakuin University, Tokyo, Japan.

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activated tin alloys. Table 1 and Photo. 2 show chemical compositions and microstructures of these tin alloys.

On the other hand, for the investigation of (2), that is, in order to make clear the behavior of molten solder to oxide films, the copper plates coated with oxide films were prepared by atmospheric oxidation at 100°C. The oxide films obtained were confirmed to

Photo. 1 Degree of wetting of pure tin and various activated tin alloys on pure copper (A) and oxidized copper with Cu_2O (400Å in thickness) (B), tested at 340°C.

Table 1 Chemical compositions of prepared tin alloys.

Alloy	Composition (wt %)			
	Li	Na	P	Sn
1	0.19	—	—	bal.
2	—	0.18	—	bal.
3	—	—	0.22	bal.

Purity of tin used is 99.99%

Photo. 2 Microstructures of the prepared tin alloys. ($\times 200 \times 2/3$)
(1) Sn-0.2%Li (2) Sn-0.2%Na (3) Sn-0.2%P

Photo. 3 Patterns obtained by electron diffraction.

(a) Cu_2O on the oxidized copper at 100°C for 30 hr.

(b) SnO_2 on the tin drop surface spreaded on the oxidized copper plate

be Cu_2O by electron diffraction analysis.

A schematic diagram of the experimental apparatus for the spreading test is shown in Fig. 1. As the atmosphere for the spreading test, high-purity dry argon with a dew point temperature of -48°C was used for copper plates without oxide films and dry argon passed through the furnace regulating the oxygen pressure (Fig. 1) was used for copper plates with oxide films. Here oxide films on the copper plates are in a state of equilibrium to the oxygen partial pressure in atmosphere. That is,

Fig. 1 Block diagram of the experimental apparatus.

- 1 : Argon gas cylinder
- 2 : Blank bottle
- 3 : Pyrogallol in alkaline solution
- 4 : conc. H_2SO_4
- 5 : Silica gel
- 6 : $\text{Ba}(\text{OH})_2$
- 7 : Gas flow meter
- 8 : Thermocouple
- 9 : Furnace for regulating oxygen pressure
- 10 : Furnace for spreading test
- 11 : Cu_2O powder
- 12 : Fitting plate for sample
- 13 : Tube for cooling water
- 14 : Quartz tube

According to eq. (1) the reaction may proceed from left to right in pure argon atmosphere: Cu_2O oxide films may be dissociated into pure copper, so that it is not capable of making the spreading test of the oxidized copper in such an atmosphere. In order to stabilize the oxide films at the experimental temperature, the reaction furnace containing high-purity cuprous oxide powder wrapped with copper foils was used. Argon passed through this reaction furnace, controlled at the same temperature as that for the spreading test furnace, protected the oxide films of Cu_2O from dissociating or reoxidizing, because argon contained a very small amount of oxygen satisfying such an equilibrium relation as expressed by eq. (1). The surface tension of liquid tin and activated tin alloys was also measured by the sessile drop method⁽¹⁰⁾⁽¹¹⁾, since the surface tension has an influence on wettability.

III. Results and Discussion

1. Effects of temperature and time on the wettability of pure tin

From Figs. 2 and 3 on the temperature and time dependence of spreading area of liquid tin on the copper plate, it is obvious that a final spreading area reaches its saturation in a relatively short time (about 3 min) at each heating temperature and no further spreading takes place with prolonged heating time. For the wetting phenomena of liquid drops on the solid surface, the following equation is generally valid when the drop of liquid is small⁽¹²⁾:

$$\gamma_s = \gamma_{ls} + \gamma_l \cos \theta, \quad (2)$$

where

γ_l : surface tension of the liquid

γ_s : surface tension of the solid

γ_{ls} : interfacial tension of the liquid/solid interface

θ : contact angle

if

$$A \gamma = \gamma_s - \gamma_{ls} = \gamma_l \cos \theta. \quad (3)$$

A is known as the adhesion tension, and the larger value of A shows the better wettability of the liquid since the surface tension γ_s before wetting changes to γ_{ls} after the surface of the solid is wetted.

In the wetting of liquid tin on solid copper, if mutual dissolution between the liquid and the solid does not occur, the spreading area of the liquid must be saturated in accordance with eq. (2), since γ_s , γ_l and γ_{ls} may be constant in this condition. The results obtained, however, show that the spreading area is not saturated instantly but has a tendency to increase continuously with heating time and finally reaches saturation. This reason cannot be explained by the temperature difference between the tin disk for

Fig. 2 Relation between the spreading area of liquid tin and reaction time.

Fig. 3 Relation between the spreading area of liquid tin and reaction temperature, reacted for 3 min.

soldering and the testing furnace, because the copper plate specimen is sufficiently preheated and moreover the heat capacity of the heating plate for the test pieces is very large.

In a reaction system accompanying such solid copper dissolution as in this experiment, parameters γ_l , γ_{ls} and θ in eqs. (2), (3) may change with heating time and temperature and consequently have influence on the spreadability. It has been made clear by our previous experiments on the reaction of copper dissolution into liquid tin that the copper concentration in liquid tin was considerably high at the interface between solid copper and liquid tin⁽¹³⁾. This phenomena might be based upon a rapid dissolution of copper into liquid tin. As the result of this dissolution reaction, the interfacial tension γ_{ls} may change with copper concentration in liquid tin, thus affecting the spreadability of liquid tin. The reaction may reach an equilibrium state after continuous dissolution of solid copper with reaction time, and so the spreadability may change continuously. Therefore the most spreaded drop may show apparently a final spreading area.

The measurement of γ_l is comparatively easy, but those of γ_s and γ_{ls} are very difficult. So, we will discuss correlatively the interfacial tension γ_{ls} in eq. (2). Figure 4 shows the spreadability of various tin-copper alloy (copper content is from 0.2 wt% to 5.0 wt%) on pure copper plates and the values of surface tension γ_l

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Fig. 4 Effects of Cu contents in the tin-copper system alloys on the spreading area and surface tension, tested at 350°C.

of these alloys. As shown in the figure, the spreading area becomes maximum at 0.6 wt% copper concentration, while the surface tension increases with copper concentration without any remarkable change at 0.6 wt% copper concentration. Since the surface tension of solid copper γ_s in eq. (3) is dependent on temperature only, it may be constant at constant temperature[†]. As shown in Fig. 4, the effect of copper concentration on the spreading area is larger than that of γ_l and consequently γ_{ls} becomes smaller in eq. (3). From the facts that γ_{ls} is changeable with copper concentration in liquid tin and A in eq. (3) is maximum at 0.6 wt% copper concentration, γ_{ls} may be minimum when the copper concentration in liquid tin reaches 0.6 wt% by the reaction of copper dissolution. As shown in Fig. 3, the temperature dependence of spreadability may similarly depend on the change of interfacial tension between the solid and the liquid. It is considered, therefore, that wetting perhaps proceeds between liquid tin-copper alloys and tin-copper system alloying layers formed by copper dissolution. In this case γ_{ls} may be the interfacial tension between the liquid tin-copper alloy and the alloying layer. As it is evident from the tin-copper system diagram⁽¹⁴⁾ that the η phase is formed at 227 ~ 415°C and the ϵ phase at 415 ~ 640°C⁽¹⁵⁾⁽¹⁶⁾, it is an important question in this experiment whether the phase adjoined to the liquid is η or ϵ .

2. Spreadability of liquid tin on the oxidized copper plates

For the investigation of effects of oxide films on copper plates, the oxidized copper plates with a definite thickness of oxide films were prepared. From Fig. 5 which shows the results of the oxidation test of copper at 100°C, it is obvious that oxide films are thickened logarithmically in the first stage and parabolically in the later stage⁽¹⁷⁾. The thickness of the oxide films provided for this experiment was

Fig. 5 Relation between the thickness of the oxide film and the oxidizing time in the oxidation of copper at 100°C in air.

Fig. 6 Relation between the spreading area of liquid tin and the thickness of the oxide film on the oxidized copper plate. Spreading limit: 90° in contact angle.

derived from Fig. 5.

The effects of oxide film thickness on the spreading area of liquid tin are shown in Fig. 6. The spreading area decreases in accordance with increase in the thickness of oxide films and the spreading limits (90° in contact angle) shift to the right side, that is, to the thicker side of oxide films. This fact indicates that oxide films on the base metal plates have a great influence upon the wettability of liquid tin. The presence of SnO_2 was recognized on the surface of tin drop after the spreading test by the electron diffraction analysis. Judging from these results, it is considered that the reducing reaction of copper oxides by liquid tin takes an important part in the spreadability. Here, the free energies of formation of Cu_2O and SnO_2 at 320°C are -30800 cal/mol and -109350 cal/mol respectively. Therefore, the following chemical reaction may easily take place if liquid tin contacts with the oxide films of Cu_2O ,

Liquid tin may not wet on solid copper until SnO_2 formed in accordance with eq. (4) is removed to float on the liquid surface. The higher the temperature, the

[†] Actual γ_s are considered to be rather a surface tension of a copper-tin alloy formed by the surface diffusion of tin.

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more easily take place this reaction, and the thicker the oxide films the smaller becomes the spreading area, because the surface tension of liquid tin may be larger owing to the formation of SnO_2 as a slag. Hence the reducing reaction of Cu_2O by liquid tin may be a very important factor for the wetting of this system.

3. Spreadability of activated tin alloy

Table 2 and Fig. 7 show the relation between temperature and the spreading area on pure copper and oxidized copper. The spreadability of the activated tin alloy on pure copper is nearly similar to that of pure tin, and this may be due mainly to the decrease of the surface tension caused by additional elements. Figure 8 shows the temperature dependence of surface tension for various activated tin alloys. As can be seen from the figure, the surface tension of activated tin alloys is slightly smaller than that of pure tin. The surface tensions of these tin alloys, in general, have the tendency to decrease with increasing temperature, being $d\gamma/dT = -0.2$ dyne/cm-deg.

The spreadability of activated tin alloys on the oxidized copper plates are largely retarded by oxide films in a similar way to the case of pure tin. The spreading limits have the tendency to shift toward the thicker side of oxide films, and this tendency differs depending on the kind of the additional element employed as the activator. The spreading area of the activated tin alloys is larger than that of pure tin on the whole, especially in the case of tin-phosphorus alloys. If the spreadability of the activated tin alloys on the oxidized copper plates is discussed in conformity with that of pure tin, the reducibility of the oxide film

Table 2 Spreading areas of liquid tin and activated tin alloys on the copper plate.

Alloy	Spreading area (mm^2/mg)			
	280°C	340°C	400°C	500°C
99.99%Sn	0.163	0.275	0.308	0.312
Sn-0.2%Li	0.178	0.294	0.315	0.320
Sn-0.2%Na	0.171	0.280	0.310	0.315
Sn-0.2%P	0.192	0.302	0.321	0.328

Fig. 7 Relation between the spreading area of various activated tin alloys and the thickness of the oxide film on the oxidized copper, tested at 340°C for 3 min.

Fig. 8 Temperature dependence of surface tension for pure tin and various activated tin alloys.

Fig. 9 Spreading limits vs temperature curves for pure tin and various activated tin alloys as functions of the thickness of the oxide film and the reaction temperature.

(Cu_2O) will be the most important factor. The properties of the activated tin alloys containing Li, Na and P as activators which are superior to pure tin are likely to make spreadability accelerate, and Li_2O , Na_2O and P_2O_5 may be produced in addition to SnO_2 by the reducing reaction of Cu_2O . The free energies of Li_2O , Na_2O and P_2O_5 at 330°C are smaller than that of Cu_2O taking the values of -125000 cal/mol, -79400 cal/mol and -291300 cal/mol respectively⁽¹⁸⁾⁽¹⁹⁾. These oxides may be rapidly formed in the activated tin alloys contacted with oxide films.

The interfacial tension between the liquid metal and the oxide formed is also an important factor affecting the spreadability, and the liquid drop in pure tin or Sn-0.2 wt%Li may be covered with SnO_2 or Li_2O in the solid state as these oxides cannot be expected to melt in this experimental condition. On the contrary, as Na_2O or P_2O_5 must be in the liquid state or sublimated, the liquid drops containing Na or P may be covered with a thin liquid film. Therefore the interfacial tension between the liquid drop and the oxide of the latter may be smaller than that of the former, that is, γ_i in eq. (3) may be smaller and consequently the spreadability is improved[†]. The tin-phosphorus alloy

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Photo. 4 The change of the shape of liquid tin drop with time for the copper and oxidized copper plates at 340°C.
(A) on the oxidized copper (B) on the pure copper

are superior in spreadability to other alloys is considered to be due to the decreases in interfacial tension between the liquid and the oxide, in addition to the small values of free energies. Figure 9 shows the spreading limits vs temperature curves for various activated tin alloys. It is obvious from the curves that liquid metals spread in the upper region and do not spread in the lower region, and have the tendency to shift to the thicker side of the oxide films than that of pure tin at low temperature, but at high temperature the activated tin alloys, except for tin-phosphorus alloys, show rather lower activity than pure tin. The reason for this may be considered as follows. The liquid metal drops are covered with SnO_2 or Li_2O (in solid state) produced by the reduction of Cu_2O and thereby the surface tension γ_l is increased; with increasing temperature, the amount of oxides increases. On the other hand, the tin-phosphorus alloy has the tendency to increase its activity with temperature. This is probably because the reducing reaction product, P_2O_5 , which is in the liquid state or sublimates at the experimental temperature, acts as a kind of flux and the interfacial tension γ_{fl} between liquid metal and P_2O_5 is decreased.

4. Mechanism of wetting

Photograph 4 shows the change in shape of the liquid drop with heating time on pure copper and oxidized copper. On the pure copper the liquid tin seems to gradually spread decreasing the contact angle without any spherical droplet, while on the oxidized copper plate the liquid tin does not spread immediately

since Cu_2O oxide films prevent the drop from spreading, but the liquid tin will follow such a wetting process as liquid tin forms a spherical droplet for a time. And the liquid tin does not spread until the reducing reaction of Cu_2O by itself, based upon the free energies of formation, proceeds. It appears that SnO_2 formed in this way floats on the liquid surface.

IV. Conclusion

The results obtained in this investigation are summarized as follows:

(1) The wettability of liquid tin on solid copper is affected by interfacial tension, depending on the amount of copper dissolved in liquid tin; the wettability increases with decrease in interfacial tension which should be minimum at 0.6 wt%Cu.

(2) Spreading tests of liquid tin and activated tin alloys on oxidized copper can successfully be carried out using a reaction furnace which keeps the oxygen partial pressure in its atmosphere above the dissociation pressure of Cu_2O to prevent the oxide films from decomposing.

(3) The spreading area of liquid tin decreases owing to the presence of oxide films. The spreading area on the oxidized copper plate with the oxide film Cu_2O (600 Å in thickness) was approximately 50% of that on pure copper at 340°C.

(4) On the oxidized copper plate the rate of spreading depends on the reduction of oxide films and the activated tin alloys containing Li, Na and P as an additional element show better wettability, most remarkably in the case of P addition.

(5) At low temperature the activated tin alloys are superior in spreading limits (90° in contact angle of the liquid) to pure tin. At high temperature these alloys are rather inferior in the limits excepting the tin-phosphorus alloy.

(6) There is a little difference in surface tension between liquid tin and activated tin alloys, and the surface tension decreases with increasing temperature in the form $d\gamma/dT = -0.2$ dyne/cm·deg.

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† For the drop of the liquid metal on the solid metal surface, covered with a thin layer of the liquid flux, the following equation is generally given:

$$\gamma_{fs} = \gamma_{ls} + \gamma_{fl} \cos \theta,$$

where, γ_{fl} and γ_{fs} are the interfacial tensions between the liquid metal and the flux, and between the solid metal and the flux, respectively. In this system the adhesion tensions between the liquid metal and the flux, and between the solid metal and the flux are represented in the forms of $\gamma_s - \gamma_{fs} = A_{fs}$ and $\gamma_s - \gamma_{ls} = A_{ls}$, respectively. The larger the adhesion tension, the better is wettability. From these relation we have: $A_{ls} = A_{fs} + \gamma_{fl} \cos \theta$. If A_{ls} and A_{fs} are considered to be constant, the smaller the value of γ_{fl} , the smaller becomes the contact angle θ , resulting in the improvement of wettability.