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Physical Meaning of Wetting Curve Traced by Meniscograph Wettability Tester (Report II)†

– Kinetic Consideration of Flux Action in Soldering –

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Abstract

The wetting curve traced by a meniscograph wettability tester was made clear physically by investigating the kinetic theory on the action of the used flux. If the oxide film on a specimen is not removed by the flux before the specimen is dipped in the solder bath, the steep part in the wetting curve, i.e. the velocity of the solder rising on the specimen is dependent only on the dissolution rate of the oxide film by the flux. On the other hand, the dissolution is the reaction of the first order and the rate constant was 0.55 ~ 0.68/sec at 503K (230°C) and 0.011 ~ 0.017/sec at room temperature and also the activation energy of the reaction was 22.2 kJ/mol.

KEY WORDS: (Solderability) (Wettability) (Wetting Rate) (Flux) (Electronics Parts)

1. Introduction

In the previous report [1], it was clarified that when the oxide film on a specimen is removed by the flux before the specimen is dipped into the solder bath, the wetting curve of the specimen is the "locus of 456K (183°C)", and the rising velocity of the solder meniscus on the specimen surface is dependent only on the heat conductivity of the specimen. From this result, it was understood that the oxide film must be removed enough by surface preparation or flux before soldering. However, in practice, it is difficult, especially, in the wave soldering process in electronics part industries, because many lead wires are oxidized extremely during packaging process.

Shipley[2] reported that the wetting rate was dependent on three parameters such as the composition of solder, the flux material and the substrate material. And, he gave the activation energy of 21.7 kJ/mol (5175 cal/mol) when the copper plate as substrate, Pb-Sn eutectic solder and the rosin alcohol solution containing 0.7% DMA HCl as flux were used for the meniscograph wettability test. However, the meaning of this activation energy was not analyzed physically and it was reported as the activation energy of the solder wetting rate.

This paper describes the physical meaning of the wetting curve when the oxide film on the specimen surface is not removed by the flux before the specimen is dipped into the solder bath. To know the physical meaning, in the first place, the reaction process that the used flux solution dissolves the oxide film was investigated, and in the second place, the reaction rate constant and its temperature dependence, i.e., the activation energy were calculated. In the third place, the value of the activation energy was compared with that of Shipley[2]. The agreement of both activation energies showed both physical meanings of the activation energy given by Shipley[2] and the wetting curve obtained in our experiment.

2. Materials and Experimental Procedures

2.1 Materials

Oxygen free copper strip of size 50(l) × 5(w) × 0.5(t) mm was used as the specimen. The surface of the specimen was polished with emery paper No. 600 and was cleaned in aceton by an ultrasonic vibrator and was then dried in air by a drier. After having been dried, each specimen was heated at 423K in air, to oxidize the specimen surface. Three kinds of heating times, i.e., 3.6, 7.2 and

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14.4 ks were selected. Therefore, four kinds of the surface conditions of specimens including non-heat-treated specimen (i.e. as emery polished specimen) were tested with a meniscograph wettability tester.

The used solder is eutectic Pb-Sn alloy (m.p.456K) and the temperature at the position of 4 mm below from the surface of molten solder was adjusted to each predetermined temperature and the surface temperature was measured by a sheathed thermocouple. Four kinds of the solder surface temperatures, i.e., 486, 499, 512 and 526K, were selected as soldering temperature.

The used flux (m.p.443K) is 35 mass% rosin alcohol solution containing DMA HCl as an activator and three kinds of Cl concentrations, i.e., 0.1, 0.2 and 0.4 mass% were selected.

2.2 Experimental methods

2.2.1 Measurement of oxide film thickness

A cathodic reduction method shown in **Fig. 1** was used to measure the thickness of the oxide film formed on each heat treated specimen. As shown in the figure, the specimen was dipped into 0.1N KCl aq. solution (temp. 303K) and a constant current (0.05 mA/cm^2) was applied between the specimen and a platinum counter electrode, and at the same time, the reducing potential at the specimen surface was recorded automatically with the reducing time by a recorder. **Figure 2** is a typical example of results obtained. In the figure, time, t, was measured graphically and the thickness of oxide film was calculated by using the following equation.

$$T = \frac{M\,i\,t}{n\,\rho\,F} \times 10^4 \qquad (1)$$

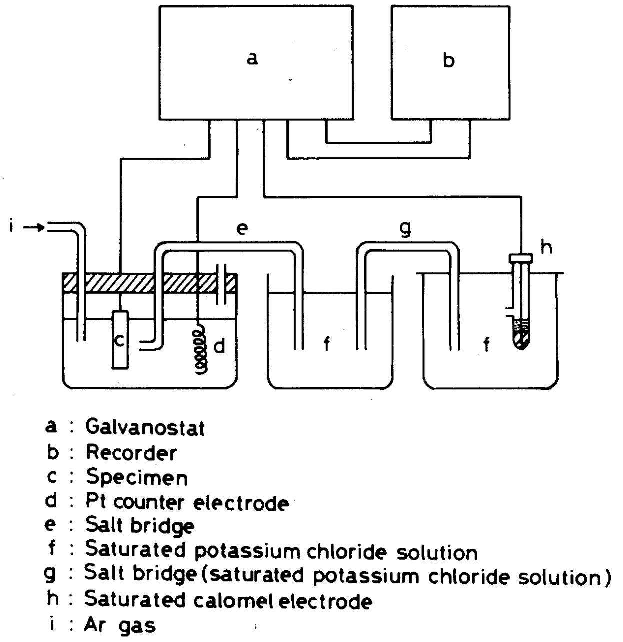

Fig. 1 Schematic of cathodic reduction apparatus.

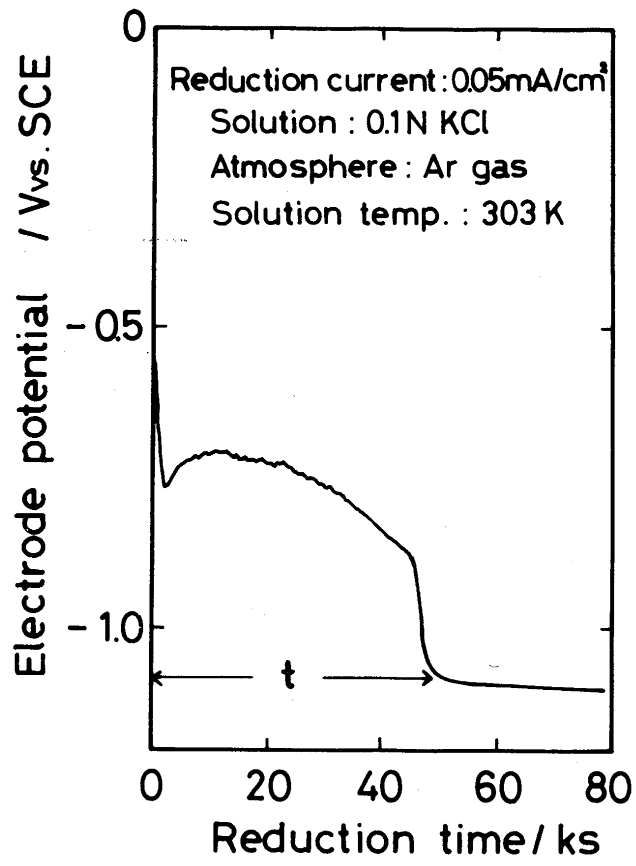

Fig. 2 Typical example of cathodic reduction curve.

where T is the thickness of oxide film (nm), i is current density (mA/cm^2), t is reducing time as mentioned above, M is molecular weight (Cu_2O: 143.09), ρ is density (Cu_2O: 6.0 g/cm^3). F is Faraday's constant and n is the number of valency.

Furthermore, the oxide film formed on the surface of heat-treated specimen was analyzed by using a X-ray diffractometer (CuKα, 40 kV, 20 mA) and the result was Cu_2O. **Table 1** lists the thickness of the oxide film formed on each heat-treated specimen and these values are the mean value of five specimens respectively.

Table 1 Thickness of oxide film formed on each heat-treated specimen.

Surface treatment		Thickness of oxide film/nm
As polished		7.8
Heat treatment	423K x 3.6ks	34
	423K x 7.2ks	47
	423K x 14.4ks	60

2.2.2 Meniscograph wettability test

Each specimen was immersed in the flux solution at room temperature for 5 sec and was then secured in the holder by the clamping screw of the meniscograph tester. The immersion speed of the specimen is 4 mm/sec, the immersion depth is 4 mm and the dipped specimen was drawn out from the solder bath after the holding time of 20 sec. **Figure 3** shows the schematic of wetting curve, as well known. In the figure, time, t_I, and force, F_w, were measured graphically. Time, t_I, is the time that the wetting of solder begins at the bottom edge of the specimen. Force, F_w, is the wetting force at equilibrium state.

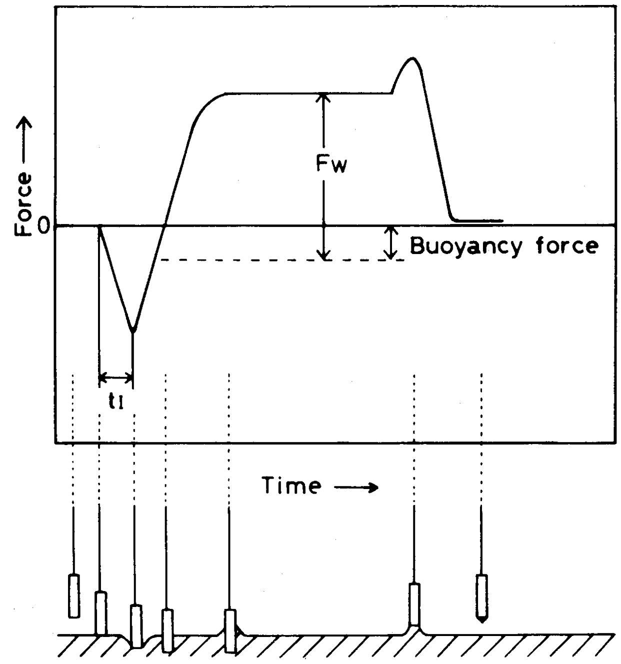

Fig. 3 Schematic of wetting curve.

3. Results and Discussions

3.1 Relation between time, t_I, and thickness of oxide film

Figures 4, 5 and **6** show the effect of the thickness of oxide film on time, t_I, when three kinds of fluxes such as the Cl concentrations of 0.1, 0.2 and 0.4 mass% were used and, as soldering temperature, four kinds of the solder surface temperatures such as 486, 499, 512 and 526K were applied in the meniscograph wettability test. As shown in these figures, time, t_I, increases with increasing the thickness of oxide film, or with decreasing the Cl concentration in the used flux and with decreasing the solder surface temperature. But, each t_I value of the film thickness 7.8 nm (i.e. as polished specimen) about each solder surface temperature shown in Fig. 4 is nearly equal to those of the film thickness 7.8 nm about those temperatures shown in both Figs. 5 and 6, irrespective to the Cl concentration of the used flux. And also, in Fig. 6, i.e. in the case of 0.4 mass% Cl, both t_I values of the film thickness 7.8 nm (i.e. as polished specimen) and of the film thickness 34 nm (i.e. 3.6 ks heat-treated specimen) at each solder surface temperature are similar. These t_I values are dependent only on the heat conductivity of the used specimen, as mentioned in the previous report[1], therefore, they are same for each solder surface temperature. On the other hand, it is believed that the oxide film formed on the specimen surface is removed fully by the flux before the specimen is dipped into the solder bath. This will be discussed again in paragraph 3.3.3.

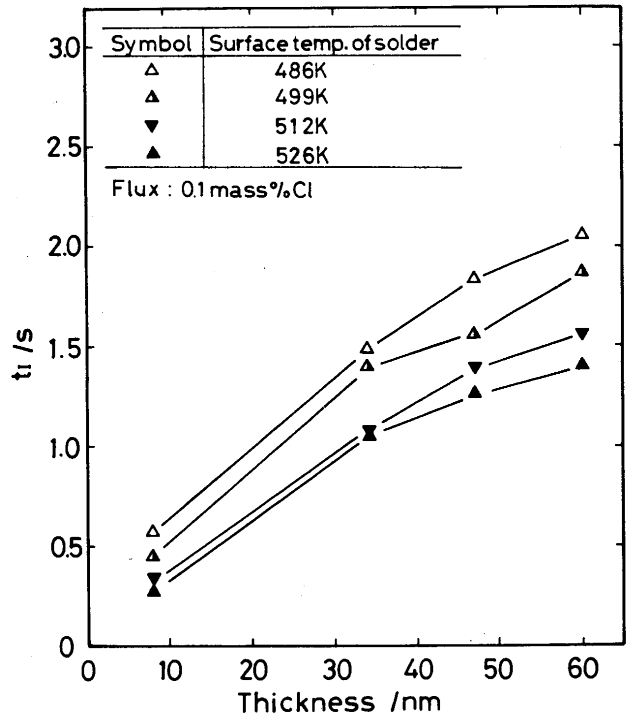

Fig. 4 Relation between t_I and thickness of oxide film (0.1 mass% Cl).

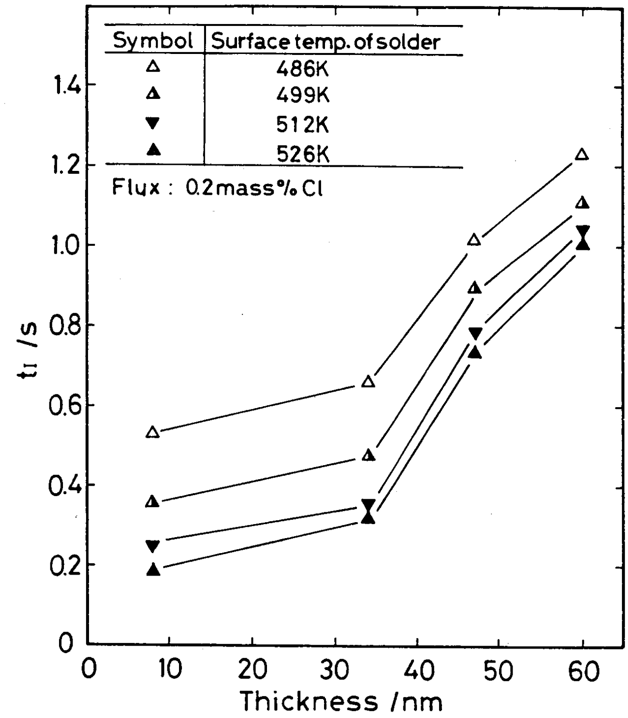

Fig. 5 Relation between t_I and thickness of oxide film (0.2 mass% Cl).

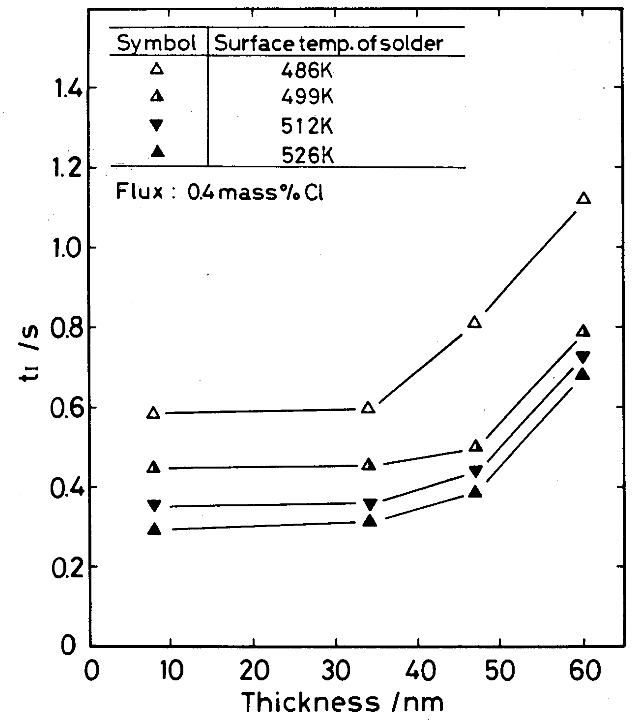

Fig. 6 Relation between t_I and thickness of oxide film (0.4 mass% Cl).

3.2 Kinetic consideration on fluxing action

Flux dissolves oxide film and if this is the reaction of the first order, the following equation is given generally.

$$-\frac{d(Y-y)}{dt} = k(Y-y)$$

By integrating,

$$k = \frac{1}{t} ln \frac{Y}{Y-y} \qquad (2)$$

where Y is the maximum thickness of the oxide film that is removed by the flux, which adheres to the specimen surface by dipping for 5 sec into the flux solution as mentioned in paragraph 2.2.2. y is the thickness of the oxide film that is removed during arbitaly time t. t is the reaction time. k is the rate constant (1/sec).

On the other hand, the used flux contains hydrochloric acid (HCl). The reaction that cuprous oxide film is removed by HCl is given by the following equation³⁾.

$$Cu_2O + 2HCl \rightarrow CuCl_2 + Cu + H_2O \qquad (3)$$

By applying this reaction, Y was calculated as mentioned below.

3.3 Calculation of rate constant, k,

3.3.1 Y, y, t and bottom edge temperature of specimen

As shown in eq.(3), 2 mol of HCl is necessary to dissolve 1 mol of Cu_2O. Therefore, in the first place, the quantity of the flux applied on the specimen was measured with a precision balance meter. In the second place, the quantity was converted in mol number of HCl. In the third place, the half of this mol number corresponds to the mol number of Cu_2O to be dissolved and it was converted in thickness dimension. **Table 2** lists the result, Y, and each value is the mean value of five specimens. From the table, the additive property of Y value for each Cl concentration is not found. This may be attributed to the quantity of the flux applied on the specimen. It is little for each flux.

Table 2 Y value and y value of each heat-treated specimen for various fluxes.

Flux	Heat treatment	Y/nm	y/nm
0.1mass%Cl	423K x 3.6ks	45	20.0
	423K x 7.2ks	45	33.1
	423K x 14.4ks	45	46.1
0.2mass%Cl	423K x 3.6ks	70	12.0
	423K x 7.2ks	70	25.1
	423K x 14.4ks	70	38.1
0.4mass%Cl	423K x 3.6ks	92	5.0
	423K x 7.2ks	92	18.1
	423K x 14.4ks	92	31.1

Table 2 also lists y values used in the calculation of k. These y values are less than the thickness of the oxide film shown in Table 1. The reason is that, as mentioned in paragraph 2.2.2, the specimen is dipped for 5 sec in the flux solution before the specimen is immersed into the solder bath, therefore, the thickness of the removed oxide film during the 5 sec is taken away from that of Table 1. Furthermore, these y values shown in Table 2 were modified owing to the following reason.

Table 3 lists the measured F_w values when each specimen was immersed into the solder bath at each solder surface temperature with the flux of 0.2 mass% Cl. As seen in the table, the F_w values decrease with increasing the solder surface temperature or with increasing the heat-treating time of specimen. **Figure 7** shows the appearance of the heat-treated specimen after having been meniscograph

Table 3 F_w value of each heat-treated specimen for each solder surface temperature (0.2 mass% Cl).

Surface temp. of solder	Heat treatment	Fw/mN
486K	as polished	3.94
	423K x 3.6ks	3.80
	423K x 7.2ks	3.61
	423K x 14.4ks	3.49
499K	as polished	3.86
	423K x 3.6ks	3.81
	423K x 7.2ks	3.69
	423K x 14.4ks	3.67
512K	as polished	3.86
	423K x 3.6ks	3.82
	423K x 7.2ks	3.72
	423K x 14.4ks	3.71
526K	as polished	3.78
	423K x 3.6ks	3.74
	423K x 7.2ks	3.80
	423K x 14.4ks	3.73

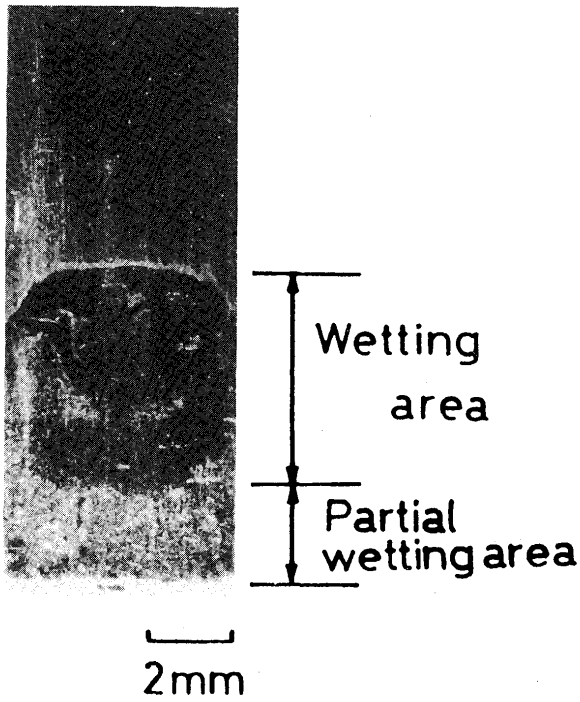

Fig. 7 Appearance of heat-treated specimen after testing.

tested. The bottom part of the specimen is partial wetting state. As mentioned in the previous report[4)], this is attributed to the hydrostatic pressure of the molten solder. Therefore, the quantity of the applied flux is insufficient to remove the thick oxide film at the bottom part. If the quantity of the flux is applied fully, i.e., if the immersion depth of the specimen is shallow, the F_w value of each specimen should be nearly equal to that of as polished specimen. Hence, eq.(2) was modified to the following equation.

$$k = \frac{1}{t} ln \frac{Y}{Y - \alpha y} \qquad (4)$$

where $\alpha (= F''_w / F'_w$; F''_w is the F_w of each heat-treated specimen and F'_w is the F_w of as polished specimen) is the ratio of wetting. In other words, the thickness of the oxide film was modified to make the same wetting state for each specimen.

Each t_I value shown in Figs. 4, 5 and 6 was used as the reaction time, t in eq.(4). The time, t_I, is the time that the wetting of solder begins at the bottom edge of the specimen, and it is the elapsed time from which the solder surface and the bottom edge of the specimen first make contact. At this elapsed time, the bottom edge temperature of each specimen having the film thickness 7.8 nm, i.e. the bottom edge temperature of as polished specimen is 456K (183°C) as mentioned in the previous report[1)]. The bottom edge temperatures of other heat-treated specimens were determined by using *Fig. 3* (*a*), (*b*), (*c*) and (*d*) shown in the previous report[1)]. For example, each t_I value of each solder surface temperature shown in Fig. 5 corresponds to the time indicated in each horizontal axis of *Fig. 3* (*a*), (*b*), (*c*) and (*d*) shown for each temperature in the previous report[1)]. **Figure** 8 shows the result obtained graphically by this method. And, this result indicates the bottom edge temperature of each specimen at each t_I shown in Fig. 5 which the Cl concentration of the used flux is 0.2 mass%. And also, in the figure, the film thickness in the horizontal axis corresponds to y value of Table 2. As seen in the figure, the bottom edge temperature increases with increasing the film thickness because the time, t_I, increases. Furthermore, *Fig. 3* (*a*), (*b*), (*c*) and (*d*) shown in the previous report[1)] will be applied also for each t_I, shown in Figs. 4 and 6, because the temperature rising of specimen is dependent only on the solder surface temperature, irrespective to the Cl concentration of the used flux. The obtained results were used to draw Fig. 11 in next paragraph.

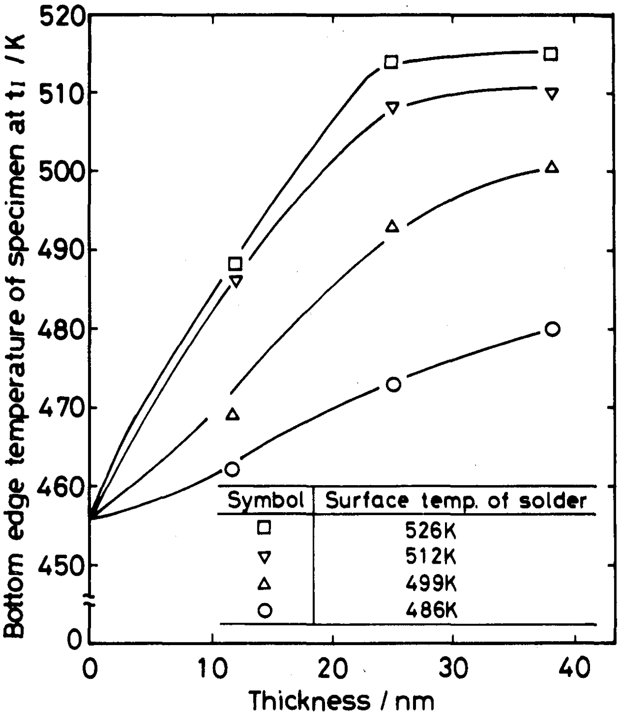

Fig. 8 Relation between bottom edge temperature of specimen and thickness of oxide film at time t_I shown in Fig. 5.

3.3.2 Temperature dependence of k

The rate constant, k, in the Cl concentration of 0.2 mass% was calculated by substituting the above mentioned Y, y, t_I and the bottom edge temperature for eq. (4). **Figure 9** shows the result, and the horizontal axis is the bottom edge temperature of specimen and dose not indicate the solder surface temperature or soldering temperature.

From Fig. 9, logarithm rate constant is plotted versus reciprocal absolute temperature as **Fig. 10**. If Arrhenius rule is realized for each calculated value in the figure, two parallel straight lines are drawn as shown in the figure. Here, two straight lines mean the upper limit and the low-

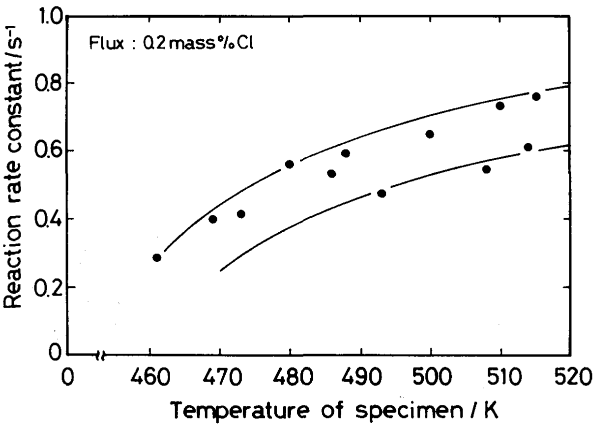

Fig. 9 Reaction rate constant at each temperature of specimen.

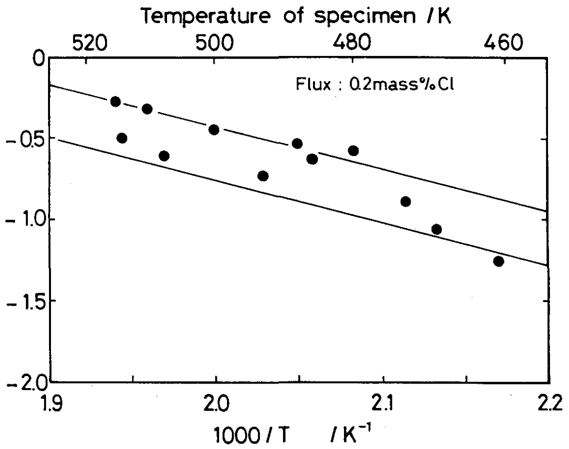

Fig. 10 Temperature dependence of rate constant (0.2 mass% Cl).

er limit of the rate constant at each temperature. **Figure 11** shows the temperature dependence of k in the Cl concentrations of 0.1 and 0.4 mass%. In the figure, two straight lines are those solves of Fig. 10. As seen in the figure, although two calculated values (at 0.0021 and 0.00215 1/k) shift from the lower straight line, it was found that Arrhenius rule is realized in Fig. 10 and also in Fig. 11. Therefore, the reaction between the used flux and the oxide film (Cu_2O) is the reaction of the first order, and the rate constant, k, is not dependent theoretically on the Cl concentration in the flux. Then, from the slopes of two straight lines, the activation energy of eq.(3) was calculated. The result was 22.2 kJ/mol. This value is the activation energy of eq.(3) during the time, t_I, shown in Fig. 3. At the time, t_I, as mentioned already, the wetting of solder begins at the bottom edge of specimen.

On the other hand, Shipley[2)] reported the activation energy that was calculated by using the slope in the steep part (from time, t_I, to equilibrium state) of wetting curve shown in Fig. 3, and the value was 21.7 kJ/mol for the Cl concentration of 0.7%. The agreement of both values shows that the meniscus rising of solder in the steep part of wetting curve is determined by the rate constant of eq.(3), i.e. the rate determining step is the dissolution of oxide film by the flux.

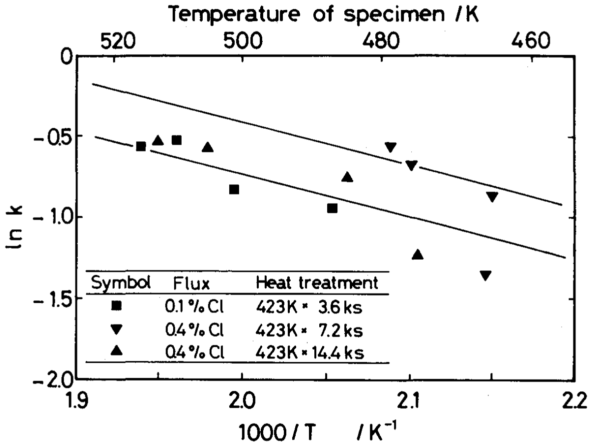

Fig. 11 Temperature dependence of rate constant (0.1 and 0.4 mass% Cl).

3.3.3 *Quantity of dissolved oxide film by flux at room temperature*

To know the rate constant of eq.(3) at room temperature (293K), an extrapolation method was applied for two straight lines shown in Fig. 10. The result was 0.017 ~ 0.011/sec. By using these values and eq.(2), the dissolution times of oxide film having the film thickness 7.8 nm (i.e. as polished specimen) with the Cl concentrations of 0.1, 0.2 and 0.4 mass% were calculated. The results were 5 ~ 17 sec. As mentioned in paragraph 2.2.2, before the specimen is dipped in the solder bath, the specimen is dipped in the flux solution for 5 sec at room temperature. Then, the fluxed specimen is secured in the holder of the meniscograph tester and is taken down and contacts the molten surface of solder. The necessary time in this procedure is about 35 sec, therefore, the time until the specimen contacts the molten surface of solder is about 40 seconds in total. This 40 seconds is longer than the calculated 5 ~ 17 sec. This proves that the oxide film of 7.8 nm shown in Figs. 4, 5 and 6 is removed fully before the specimen contacts the molten surface of solder, as mentioned in paragraph 3.1. And also, in the case of the film thickness 34 nm (heat-treated specimen at 423K for 3.6 ks) shown in Fig. 6, the dissolution times 24 ~ 41 sec were calculated by the same method. These values also justify that the oxide film on the specimen is removed fully. As mentioned in paragraph 3.1, each time, t_I, of these specimens is about equal values for each molten solder surface temperature, namely, the rate determining step is the thermal diffusivity of the used specimen as mentioned in the previous report[1)].

4. Conclusions

When the oxide film on the specimen is not removed by the flux before the specimen is dipped in the solder bath, the physical meaning of the wetting curve traced by the meniscograph tester was made clear by investigating the kinetic theory on the action of the used flux. The results are summarized as follows;

1) The reaction that the used flux dissolves the oxide film (Cu_2O) is given by eq.(3) and this is the reaction of the first order. The rate constant at each temperature is given in Fig. 9, furthermore, the rate constant at room temperature is 0.017 ~ 0.011/sec. The temperature dependence of the rate constant, i.e. the activation energy of eq.(3) was 22.2 kJ/mol.
2) The above 22.2 kJ/mol agreed with that of Shipley[2]. From this agreement, the physical meaning of the steep part in the wetting curve was made clear. Namely, the rising velocity of solder from the bottom edge of the specimen to the equilibrium state is dependent on the dissolution rate of oxide film by the used flux.
3) When the oxide film on the specimen is removed before dipping in solder bath, the rate determining step of the solder rising is the heat conductivity of the used specimen. On the other hand, when the oxide film is not removed before dipping, the rate determining step of the solder rising is the dissolution rate of the oxide film by the flux. From these results, the velocity that the solder wets the specimen is concluded to be very fast, i.e. the wetting occurs instantaneouslly when the eutectic Pb-Sn solder contacts the copper specimen at 456K (183°C).

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References

1) I. Okamoto, T. Takemoto, M. Mizutani and I. Mori: Physical Meaning of Wetting Curve Traced by Meniscograph Wettability Tester, Trans. of JWRI, Vol. 14 (1985) No. 1, 21–27.

2) J.F. Shipley: Influence of Flux, Substrate and Composition on Solder Wetting, Weld. J., Vol. 54 (1975) No. 10, 357s–362s.

3) R.J. Klein Wassink: Soldering in Electronics, Electrochemical Publications Ltd., (1984), 146.

4) I. Okamoto, A. Ohmori and Y. Fukada: Occurrence of Non-Wetted Parts in Dip Soldering (Report-1), Trans. of JWRI, Vol. 9 (1980) No. 1, 19–25.