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Effect of Flux Composition on Wettability in Soldering of Aluminum†

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Abstract

The effect of flux composition on wettability for soldering of aluminum has been investigated by the use of a wetting balance method. Wettability was measured mainly by the wetting time, T_w, *using Sn-9 mass% Zn solder and A1100 aluminum base metal. Fluxes used were composed of triethanolamine-ammonium fluoroborate; and the effects of additional reagents such as metal fluoborates were investigated. Increase of solder bath temperature (T) decreased* T_w. *The plots between* $\ln(1/T_w)$ *and* $1/T$ *showed straight relationships. The apparent activation energies calculated from the gradients of the straight lines ranged between 27.7~70.0 kJ/mol depending on the flux composition. After the wettability test, metal was precipitated on the surface of aluminum base metal from the added borofluorides in the fluxes. Precipitated metals with low melting points were found to be effective in shortening* T_w. *On the contrary,* T_w *increased with a rise of the melting point of precipitated metal.*

KEY WORDS: (Wettability) (Aluminum Alloys) (Soldering) (Flux Composition) (Wetting Balance)

1. Introduction

The use of aluminum in electronic assemblies is increasing, but the joining of aluminum, especially in soldering is rather difficult due to its stable surface oxide film. From the point of view of the heat resistance of electronic packages and productivity, soldering would be one solution for low temperature joining. Fluxless soldering is the best method for the chemical reliability of the joints, however, the supply of pressure or ultrasonic power is necessary[1-3]. As a result, various metallization processes are required to improve solderability with Sn-Pb solders, but these metallization processes raise the cost of products. Accordingly, direct soldering without metallization of aluminum would be the best choice. For this purpose the use of soldering fluxes with appropriate compositions would be advantageous. Among many solderability tests[4], the wetting balance (surface tension) method can indicate the changes of the wetting force during the soldering stage, thus give information about the dynamic reaction between molten solder and solid base metal. The method is effective for the selection of fluxes, solders, base metals, soldering conditions and appropriate combinations among these factors[5-10]. The present work aimed to investigate the effects of composition of soldering flux on wettability of aluminum using the wetting test.

2. Materials and Experimental Procedures

2.1 Materials

Wetting tests were conducted with Sn-9 mass% Zn solder, A1100 base metal and fluxes made of triethanolamine-ammonium fluoroborate. Base aluminum was A1100-H14 plate with dimensions of 50^lx5^wx0.5^t mm. Specimens were used without any surface treatment except degreasing in an ultrasonic acetone bath. Specimens for SEM observations were electro-polished before the wetting test to reveal the front of wet solder on the base metal.

Sn-9 mass% eutectic solder(AH-S91Z, JIS Z 3281, eutectic temperature: 198.5 °C) was made from high purity metal with 99.999 mass% Sn and 99.99 mass% Zn. Solder bath temperatures were selected to be 30 °C above the eutectic temperature.

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Table 1 Chemical compositions of aluminum soldering fluxes.

Flux	Base compositions (g/kg)			Additional reagents (mol/kg)			
Number	$(C_2H_4OH)_3N$	NH_4BF_4	H_2O	$Cd(BF_4)_2$	$Sn(BF_4)_2$	$Zn(BF_4)_2$	HBF_4
1	728	71	113	0.31	—	—	—
2	728	71	111	—	0.31	—	—
3	728	71	127	—	—	0.31	—
4	728	71	146	—	—	—	0.62
5	911	89	—	—	—	—	—

Table 1 shows the composition of fluxes. Base chemicals are triethanolamine(TEA), ammonium fluoroborate, water and additional reagents of metal borofluorides. Concentrations of additional reagents are 0.31 mol/kg for metal borofluorides, and 0.62 mol/kg for hydrofluoroboric acid. In all fluxes the gram equivalents of additional reagents are the same.

2.2 Wetting balance method

Figure 1 shows the typical wetting force-time curve and corresponding state of solder and specimen. Various parameters have been proposed in the wetting force-time curve [5,6], however, in the present work, the wetting time (T_w) was adopted as the wettability parameter and the wetting force (F_w) was also compared in some cases. F_w was the maximum value of the test within the immersion time of 10 s. T_w was measured at the point where the wetting force returned to 0 value. Neither values contain the buoyancy correction of about 70 mg for a 4 mm immersion depth. In the wetting balance method, wettability is considered to be good at shorter T_w times and larger F_w forces.

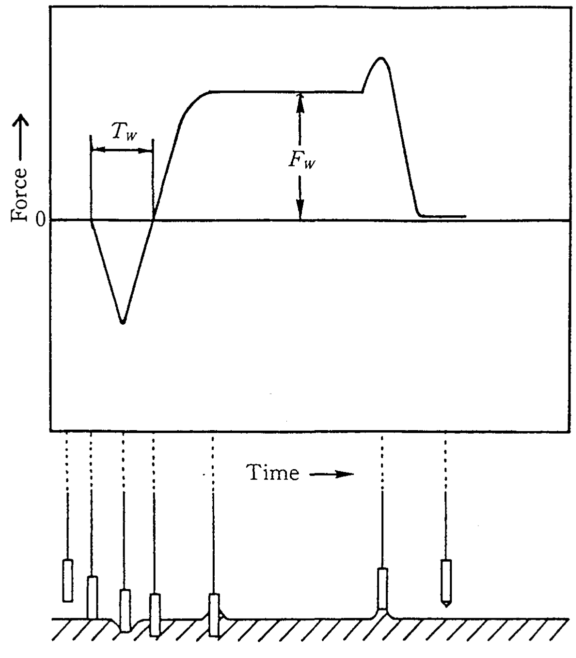


Fig. 1 Typical wetting curves and corresponding state of solder and specimen.

A wetting balance tester (Solder Checker SAT-2000, RHESCA Corporation) was used to evaluate wettability.

3. Results

3.1 Factors Influencing Wetting Time

There are many factors influencing the wetting time in a wetting balance test. Among these, some important factors to establish the experimental procedures were selected and were evaluated by a statistical factor analysis. The selected factors are Group A; additional chemical reagents to flux, Group B; immersion time of specimen in solder bath, and Group C; immersion rate of specimen into solder bath, and Group D; immersion depth. Each factor is classified as follows; A_1; $Cd(BF_4)_2$, A_2; $Sn(BF_4)_2$, A_3; $Zn(BF_4)_2$, B_1; 5 s, B_2; 10 s, C_1; 2 mm/s, C_2; 4 mm/s, D_1; 2 mm, D_2; 4 mm. For this test the solder bath temperature was fixed at 250 °C, the base metal was A1100 aluminum with the as-received surface degreased in an acetone bath.

The combinations of test factors and measurements of T_w are indicated in **Table 2**. The analyzed data are also shown in **Table 3**. Among these four factors, group A had the dominant effect by the F' value with the risk percentage of 1 % as indicated by the mark **.

The immersion time in flux has little effect within the range of the present experimental conditions, therefore, the reaction between aluminum base metal and soldering flux could be ignored at room temperature within the immersion time up to 10 s. The immersion rate into the solder bath also has little influence. But the immersion depth has a distinct influence, with the risk percentage of 5 %. It is found that the interaction among the other factors could be ignored, because the F test values are extremely small, below 1.

The wetting time with a 4 mm immersion is longer than with a 2 mm immersion, therefore, the wettability is more easily distinguished with the 4 mm immersion depth. From the data obtained, the following experimental conditions were selected if not mentioned,

Table 2 Combination of various test parameters and measured wetting time (T_w).

No.	A	B	C	D	T_W (s)	
1	A_1	B_1	C_1	D_1	1.40	1.80
2	A_1	B_1	C_1	D_2	1.76	2.04
3	A_1	B_1	C_2	D_1	1.56	1.98
4	A_1	B_1	C_2	D_2	1.74	1.98
5	A_1	B_2	C_1	D_1	1.52	1.76
6	A_1	B_2	C_1	D_2	2.00	1.96
7	A_1	B_2	C_2	D_1	1.78	1.82
8	A_1	B_2	C_2	D_2	1.72	1.84
9	A_2	B_1	C_1	D_1	1.50	1.56
10	A_2	B_1	C_1	D_2	1.62	1.60
11	A_2	B_1	C_2	D_1	1.42	1.52
12	A_2	B_1	C_2	D_2	1.58	1.56
13	A_2	B_2	C_1	D_1	1.48	1.48
14	A_2	B_2	C_1	D_2	1.56	1.62
15	A_2	B_2	C_2	D_1	1.36	1.46
16	A_2	B_2	C_2	D_2	1.58	1.62
17	A_3	B_1	C_1	D_1	1.82	2.68
18	A_3	B_1	C_1	D_2	2.10	2.44
19	A_3	B_1	C_2	D_1	2.32	2.32
20	A_3	B_1	C_2	D_2	2.00	2.74
21	A_3	B_2	C_1	D_1	1.82	2.28
22	A_3	B_2	C_1	D_2	2.30	2.28
23	A_3	B_2	C_2	D_1	2.16	2.60
24	A_3	B_2	C_2	D_2	2.06	3.12

A ; Composition of flux A_1 : $Cd(BF_4)_2$
A_2 : $Sn(BF_4)_2$
A_3 : $Zn(BF_4)_2$
B ; Immersion time in flux B_1 : 5 s
B_2 : 10 s
C ; Immersion speed C_1 : 2 mm/s
C_2 : 4 mm/s
D ; Immersion depth D_1 : 2 mm
D_2 : 4 mm

B; 5 s, C; 4 mm/s, D; 4 mm. As shown in Table 2, the date obtained scattering in some experiments, in these cases the experiment was repeated at least 6 times and the data indicated are the mean values.

The established experimental sequences of the surface tension method are illustrated in **Fig. 2**. At the first stage, a specimen was immersed into a flux to half its length for 5 s, after which it was withdrawn from the flux bath and set vertically on a holder. After cleaning the surface of the molten solder to remove surface oxide films the specimen was moved downwards, to touch the molten solder and immersed to 4 mm in depth. After immersion for 10 s the specimen was removed. The immersion rate was 4 mm/s. The elapsed time of each process is also indicated in Fig. 2. It is important to maintain the sequential time identical for each test to avoid the scattering of data.

3.2 Effect of Flux Composition and Solder Bath Temperature

Figure 3 shows the wetting time (T_w) of 1100 alloy with the as received surface. A rise of solder bath temperature decreased T_w in all cases. Additions of $Sn(BF_4)_2$, HBF_4 and $Cd(BF_4)_2$ enhanced wetting, especially at lower temperatures. However, addition of $Zn(BF_4)_2$ lowered wettability. The curves did not cross each other, therefore, the efficacy of soldering flux could be compared at each temperature. The difference in T_w depending on the flux composition could be most easily distinguished at lower temperature. Accordingly, conduct of the wetting test at lower temperatures is recommended for a wetting balance method.

From Fig. 3 the order of the additional reagents from shorter to longer T_w is as follows.

$$Sn(BF_4)_2 < HBF_4 < Cd(BF_4)_2 < \text{No Addition} < Zn(BF_4)_2$$

It is also obvious from Fig. 3, the flux with the longer T_w, and poor wettability, shows the largest dependence of T_w on solder bath temperature.

The plots between $\ln(1/T_w)$ and $1/T$ showed straight lines as indicated in **Fig. 4**. From the gradients of these lines the activation energy is obtained. As indicated in **Table 4**, the calculated values are 43.8, 30.4, 70.0, 36.6 and 48.7 kJ/mol for fluxes No. 1, 2, 3, 4 and 5 respectively. The activation energy follows the temperature dependence of T_w, therefore, the value became large in longer T_w.

Figure 5 shows the scanning electron micrographs of specimens tested at 268 °C. The observed area was the front of the solder wetting the aluminum specimen. In No. 4 flux, with the addition of HBF_4, severe corrosion of aluminum base metal was observed. In No. 5 flux without the additional reagents, pits were found, the diameters of which are almost a few μm. In fluxes with additional reagents of metal borofluorides, deposits are observed. The energy dispersive characteristic X-ray analysis (EDX) revealed that these deposits contained Cd, Sn, and Zn for No. 1, 2 and 3 fluxes respectively (**Fig. 6**), suggesting the deposition from metal borofluorides in fluxes [11]. Of course the deposition of metal could not be detected in fluxes No. 4 and 5 fluxes, although, enhanced fluxing action by the addition of HBF_4 is confirmed. The following electrochemical reactions are suggested to be occurring during the wetting test.

Anodic reaction: $Al \rightarrow Al^{3+} + 3e$ (1)
Cathodic reaction: $M^{n+} + ne \rightarrow M$ (2)
(M: additional metal in metal borofluoride,
n: valence)

$2H^+ + 2e \rightarrow H_2$ (3)

Table 3 Results of analysis on various test parameters.

	S	ϕ	V	F	F'
A; Flux	5.08571	2	2.54286	37.561	51.88**
B; Immersion time in flux	0.00041	1	0.00041	0.006	0.008
C; Immersion speed	0.04441	1	0.04441	0.656	0.906
D; Immersion depth	0.24367	1	0.24367	3.599	4.972*
A×B	0.00582	2	0.00291	0.043	
A×C	0.12402	2	0.06201	0.916	1.265
A×D	0.00755	2	0.00378	0.056	
B×C	0.00908	1	0.00908	0.134	
B×D	0.01541	1	0.01541	0.228	
C×D	0.01841	1	0.01841	0.272	
A×B×C	0.05145	2	0.02573	0.380	
B×C×D	0.00187	1	0.00187	0.028	
C×D×A	0.06531	2	0.03266	0.482	
B×A×B	0.02551	2	0.01276	0.188	
res	1.76015	26	0.06770		
res′	1.96056	40	0.04901		
	7.45878	47			

S: deviations, ϕ; degree of freedom, V: variance, res; res′: residues, F: F value $= V/V_{res}$, F': F' value $= V/V_{res'}$

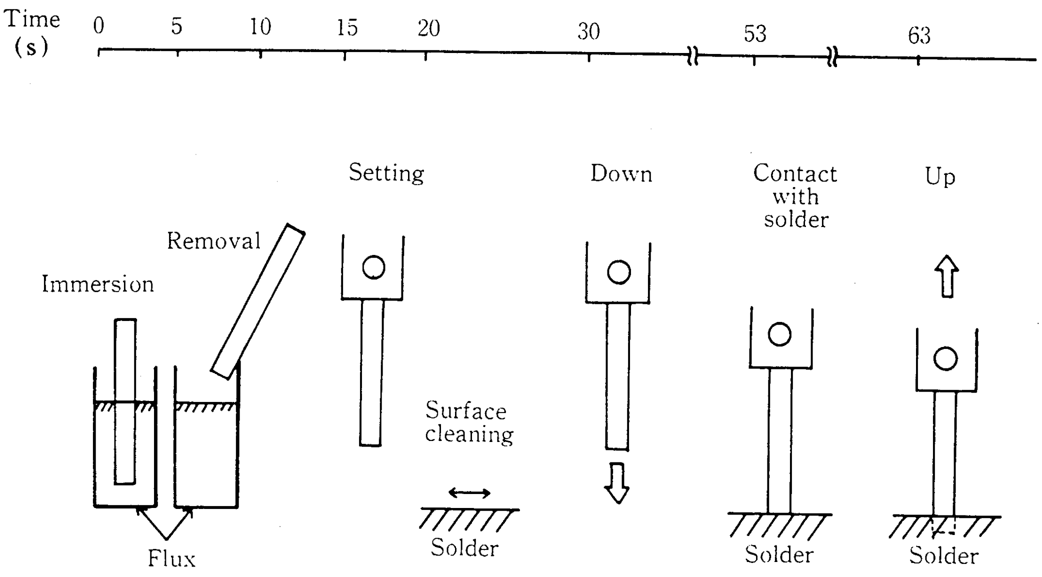


Fig. 2 Experimental procedures for solderbility test using a surface tension method.

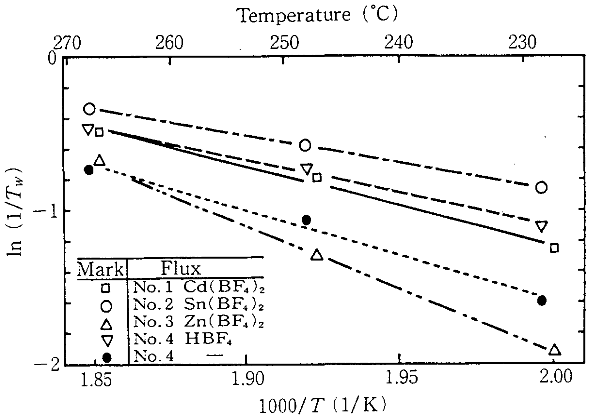


Fig. 3 Effect of solder bath temperature and soldering flux composition on wetting time.

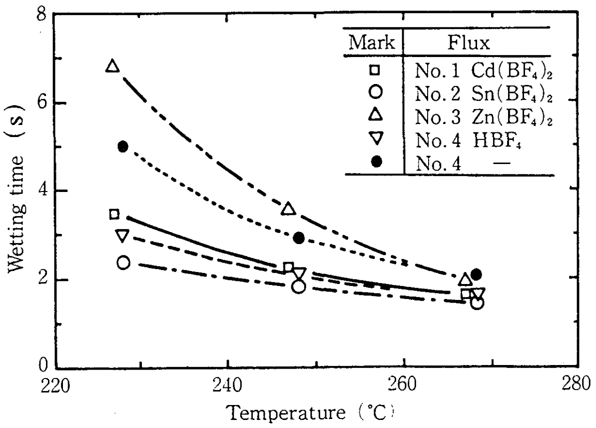


Fig. 4 Plots of ln(1/T_w) vs. 1/T: T_w; wetting time, T; solder bath temperature (K).

Table 4 Activation energies for various fluxes calculated by inverse value of wetting time (T_w).

Flux	Additional reagent	Activation energy (kJ/mol)
No. 1	$Cd(BF_4)_2$	43.8
No. 2	$Sn(BF_4)_2$	30.4
No. 3	$Zn(BF_4)_2$	70.0
No. 4	HBF_4	36.6
No. 5	—	48.7

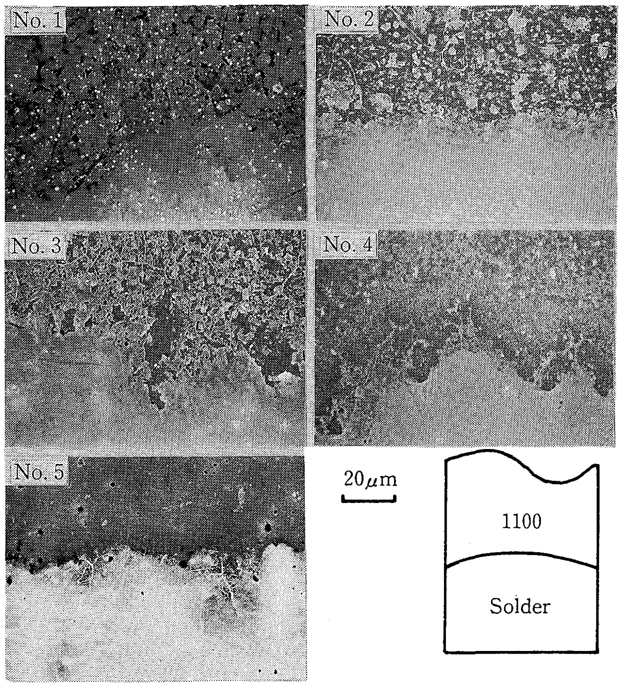


Fig. 5 Scanning electron micrographs of interface of solder/1100 aluminum base metal, numbers show used fluxes.

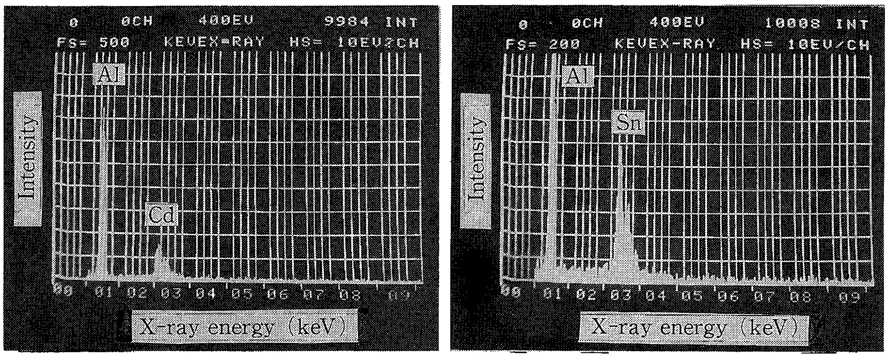
4. Discussion

4.1 Effect of basic flux composition

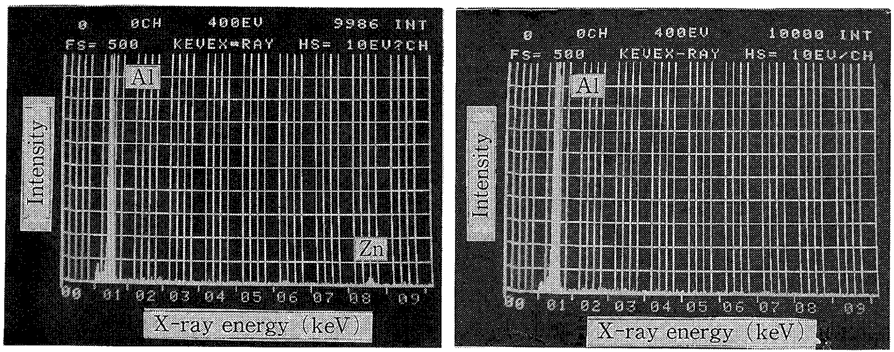
In the present experiment the main constituents of soldering flux are triethanolamine (TEA) and ammonium fluoroboride, to which various metal fluoroborates are added. To confirm the role of each constituent, the effect of basic reagents was investigated separately.

Figure 7 shows the wetting curves of aluminum tested by various fluxes. It is clear that TEA did not wet aluminum with Sn-Zn solder. The addition of water to TEA also showed no wetting. The addition of ammonium fluoroborate induced wetting, and the addition of water slightly prolonged the wetting time and lowered the wetting force, thus the addition of water slightly lowered the wettability. The addition of HBF_4 showed good wetting. From Fig. 7, it is evident that since the added fluoroborate gave wettability, the role of the reagent should be as follows.

i) Remove the surface oxide of aluminum base metal and molten solder reacting with them by an electrochemical process. This includes the following two processes; reduction of Al_2O_3 and the mechanical removal by dissolution of aluminum beneath the oxide film.



(a) Flux : No. 1 Cd $(BF_4)_2$ (b) Flux : No. 2 Sn $(BF_4)_2$



(c) Flux : No. 3 Zn $(BF_4)_2$ (d) Flux : No. 4 HBF_4

Fig. 6 EDX analysis of soldered 1100 aluminum surface.

ii) Enhancement of wetting by the precipitation of wettable metal from the flux on to the base metal surface.

The reaction i) is the surface cleaning by electrochemical anodic dissolution of aluminum. The added fluoroborate reacts with oxide by the following equation.

$$BF^{4-} \rightarrow BF_3 + F^- \qquad (4)$$

$$Al_2O_3 + 6F^- \rightarrow 2AlF_3 + 3O^{2-} \qquad (5)$$

The reaction ii) involves cathodic reaction by Eq. (2), surface modification through precipitation of metal from flux, and for this purpose the precipitation of tin was the best choice from the present experiment.

4.2 Effect of metal fluoroborate

The efficacy of flux can be determined by the reaction rate of eqs. (1)~(3). In the present study various metal borofluorides were added to flux and the metal precipitated on aluminum surface from the borofluorides. The ease of the precipitation reaction could be estimated from the standard electrode potential. The standard electrode potentials of metals in borofluorides are lowered in the following order; Sn, Cd, Zn. That is also the order of ease of precipitation, corresponding to the order of the shorter wetting time.

The order also coincides with the melting points of precipitated metals. **Figure 8** shows the plots of the melting point of added metal in borofluoride and T_w. The contents of metal borofluorides are 1.1 and 2.2 mol%. Other metal borofluorides such as $Pb(BF_4)_2$, $Cu(BF_4)_2$ and $Fe(BF_4)_2$ were added to TEA, NH_4BF_4 and H_2O base flux with the following mol%; 36.6: 5.1: 58.3. The flux composition in this test was slightly different from that in Table 1. T_w becomes longer with increasing melting point of the metal in additional borofluorides at both concentrations. On the other hand, the standard electrode potential rises in the following order; Zn, Fe, Cd, Sn, Pb, Cu, for divalent ions respectively. There is no relation between the standard electrode potential and T_w.

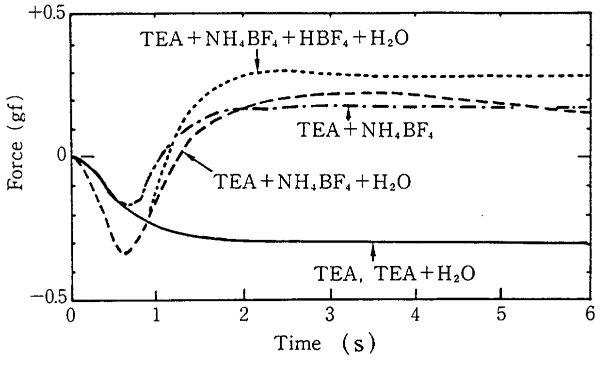


Fig. 7 Wetting curves of pure aluminum base metal using various flux compositions.

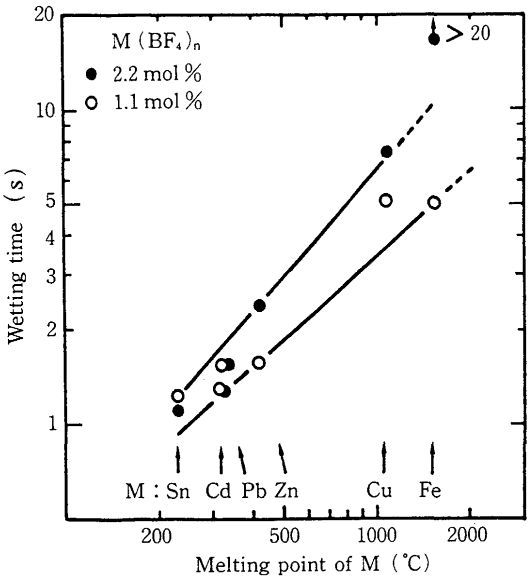


Fig. 8 Plots of melting point of added metals into fluxes vs. wetting time (T_w).

The following reasons for the difficulty of wetting in metal borofluorides with higher metal melting points might be considered. The amount of precipitation is low, the reaction between aluminum and precipitated metal is low and/or the precipitated metal is not wetted by the molten solder. Accordingly, the addition of metal borofluorides with low melting point metal is more effective in improving the wettability of aluminum.

5. Summary

The effect of soldering flux composition on wettability of aluminum was investigated using a wetting balance method, Sn-9 mass %Zn solder and triethanolamine-ammonium fluoroborate fluxes. The results obtained are summarized as follows.

(1) The wettability of aluminum could be easily distinguished by a wetting balance method and the method is useful for determining the efficacy of flux for soldering of aluminum.

(2) Wettability was markedly influenced by the kinds of metal borofluorides added to the soldering flux. The addition of low melting point metal borofluoride is preferable to enhance wettability.

(3) Wetting time decreased with increasing solder bath temperature and the plots between ln $1/T_w$ vs.$1/T$ showed straight relations. The activation energies calculated from the gradients of the plots depended on the flux composition and ranged from 27.7 to 70.0 kJ/mol.

(4) The wettability depended on the kind of precipitated metal from the borofluoride, and the precipitation of low melting point metal markedly improved wettability of aluminum with Sn-9 mass %Zn solder.

(5) TEA alone in flux does not confer wettability which only arises through the further addition of fluoroborate.

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