Studies on Flux Action of Silver Brazing (Report I) †
—— Metallic Chlorides ——

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Abstract

When metallic chloride was used as flux during brazing, not only the reactivity between molten filler metal and metallic chloride, but also the affinity of base metal with metal element of metallic chloride, played a very important part in spreading of filler metal on Cu or Fe plate.

The reaction between metallic chloride with BAg-1 or BAg-5 alloy occurs as follows;

$$Zn - (BAg-1 \text{ or } BAg-5) + MCl_2 \xrightarrow{\Delta} ZnCl_2 + M - (BAg-1 \text{ or } BAg-5)$$

1. Introduction

In previous paper[1-4], it has been reported on the relation between the spreadability of Sn and the reaction (eq-1) of molten Sn with inorganic metallic salt or the dissolution of metal element from metallic salt in Sn, when various metallic salts were used as flux and Sn as solder.

$$\text{M salt} + \text{Sn} \xrightarrow{\Delta} \text{Sn salt} + \text{M} - (\text{Sn}) \quad \text{----------} \quad (1)$$

It was shown that the above reaction(eq-1) was dependent on electro-chemical series of metal in molten salt. Then, it was elucidated that the better the reactivity between metallic salt and Sn was, the larger the spreading became. In the case of brazing, it may be anticipated that the reaction between metallic chloride and Zn occurs, since Zn is the most base when BAg-1 alloy is used, and that the spreading is promoted by the reaction.

In this report, the flux action of various metallic chlorides on brazing was studied, emphasizing the reaction between molten BAg alloy and metallic chloride on the spreadability in order to obtain a flux containing no fluorides but with similar effect as flux bearing fluorides.

2. Experimental apparatus and procedure

The apparatus used for spreading test is shown in Fig. 1, and tests were done as follows; BAg alloy (0.1 g) (BAg-1 and BAg-5) and flux (0.2 g) are placed quietly on base metal in quartz tube, and the specimens were heated at 700°C or 800°C and kept at the temperature for one min. in electric furnace. Commercially available reagent grade various metal chlorides as shown in Table 1 were used as flux, and BAg alloy (BAg-1 and BAg-5) used are shown in Table 2.

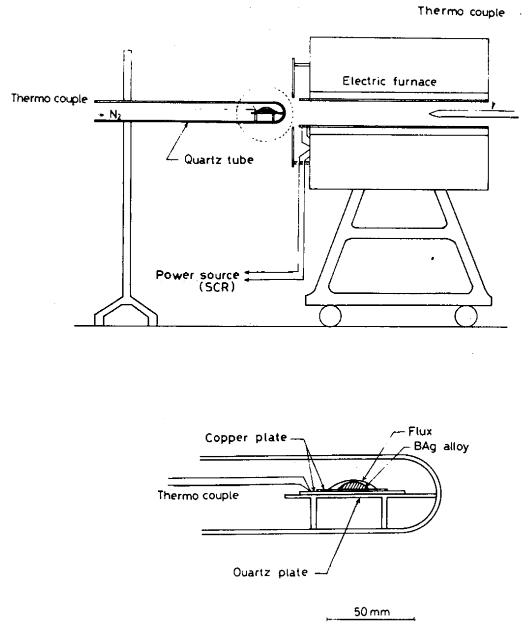

Fig. 1 Apparatus for spreading test

Cu (JIS CuP-1) and armco iron were used as base metal. The dissolution of metal element from metallic chloride to BAg alloy was elucidated by EPM analyzing the cross section of specimens after spreading test.

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Table 1 Melting pt. and boiling pt. of chlorides used as flux

various chlorides	m.p., (°C)	b.p., (°C)
$PdCl_2$	680	(1200)
AgCl	455	1564
$CoCl_2$	740	1025
$CdCl_2$	568	961
CuCl	430	1690
$FeCl_2$	677	1012
KCl	772	1510
LiCl	610	1681
$NiCl_2$	1030	(1740)
$SnCl_2$	247	652
$ZnCl_2$	318	732
40KCl-60LiCl eutectic	356	——

Table 2 Chemical compositions of BAg filler metals

Alloy	Chemical composition, wt%				Brazing temp. (C)
	Ag	Cu	Zn	Cd	
BAg-1	44-46	14-16	14-18	23-24	620-760
BAg-5	44-46	29-31	23-27	——	745-845

3. Results and Discussions

3.1 Flux action of metallic chloride on brazing on Cu plate and Fe plate

In order to know the effect of metallic chloride on brazability, comparably heat stable KCl-LiCl salt was used as base flux, since each metal element in BAg-1 or BAg-5 alloy scarcely reacts with the eutectic salt. Metallic chloride added to the eutectic salt, which contains comparably more noble metal was chosen.

The results of spreading tests on Cu plate are shown in Fig. 2 and Fig. 3, respectively for BAg-1 and BAg-5 alloys, when various metallic chlordies are used as flux. From Fig. 2 and Fig. 3, the addition of metallic chloride to the eutectic salt shows the remarkable increase of spreading in comparison with the case without metallic chloride.

On brazing, the elimination of oxide films on Cu plate is important. When the above eutectic salt is used as flux, partial wetting occurs on Cu plate, and the elimination of oxide films on Cu plate is due to the reaction (eq.3)[5]

$$CuO \longrightarrow Cu^{++} + O^{=} \quad (3)$$

However, the effect of metallic chloride of comparatively noble metal on brazability was observed to be different. The difference may be due to that of the reactivity between metallic chloride and BAg alloy, namely that of dissolution of metal element in BAg alloy from metallic chloride.

So, the dissolution of metal element into BAg-1 or BAg-5 alloy from metallic chloride was investigated by analyzing the cross section of specimens by EPMA, in order to elucidate the addition effect of metallic chrolide to the base flux on spreading of BAg alloys.

In Table 3 and Table 4, the dissolution of metal from flux are shown, respectively for BAg-1 and BAg-5 alloys. The amount(%) of metal dissolved in BAg alloy was given by the relative X-ray intensity ratio. Moreover, the results of line analysis by EPMA are shown in Fig. 4 and Fig. 5, respectively in the case of BAg-1 and BAg-5 alloys with $10wt\%NiCl_2$-$90wt\%LiCl/KCl$ eutectic system

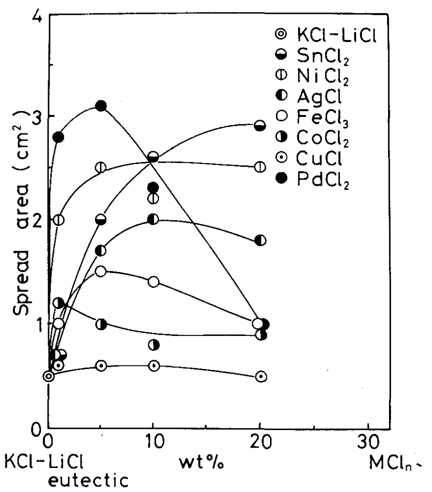


Fig. 2 Spread area of BAg-1 on Cu plate at 700°C for 1 min. vs. used flux composition

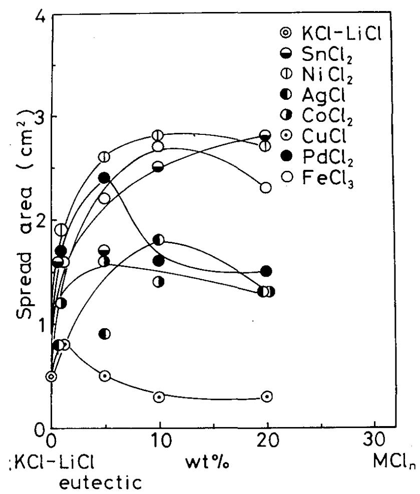
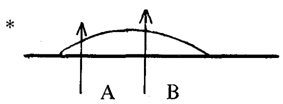


Fig. 3 Spread area of BAg-5 on Cu plate at 800°C for 1 min. vs. used flux composition

Table 3 Dissolution amount of metal containing in flux into BAg-1 spread on Cu plate

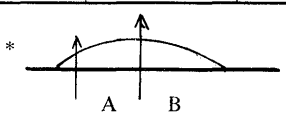
Flux	Analyzed position*	Dissolution amount** of metal from flux (%)
10 wt% $SnCl_2$	A	4
	B	6 (uniformly)
10 wt% $PdCl_2$	A	6
	B	9 (uniformly)
10 wt% $NiCl_2$	A	3
	B	20 (at surface) 2 (uniformly) 13 (at interface)
10 wt% $FeCl_3$	A	2
	B	trace amount
10 wt% $CoCl_2$	A	5
	B	8 4 (at random)



** relative x-ray intensity ratio by EPMA

Table 4 Dissolution amount of metal containing in flux into BAg-5 spread on Cu plate

Flux	Analyzed position*	Dissolution amount** of metal from flux (%%)
10 wt% $NiCl_2$	A	7
	B	3 (uniformly)
10 wt% $ReCl_3$	A	15
	B	13
10 wt% $SnCl_2$	A	7
	B	4 (uniformly)
10 wt% $PaCl_2$	A	7
	B	11 (uniformly)
10 wt% $CoCl_2$	A	4
	B	2 (uniformly)



** relative x-ray intensity ratio by EPMA

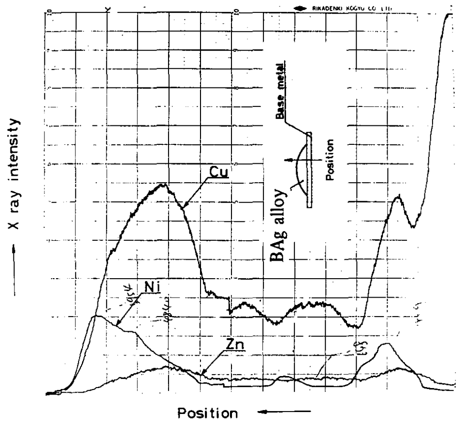


Fig. 4 Distribution of Ni in BAg-1 spread on Cu plate, using 10wt% $NiCl_2$ as flux

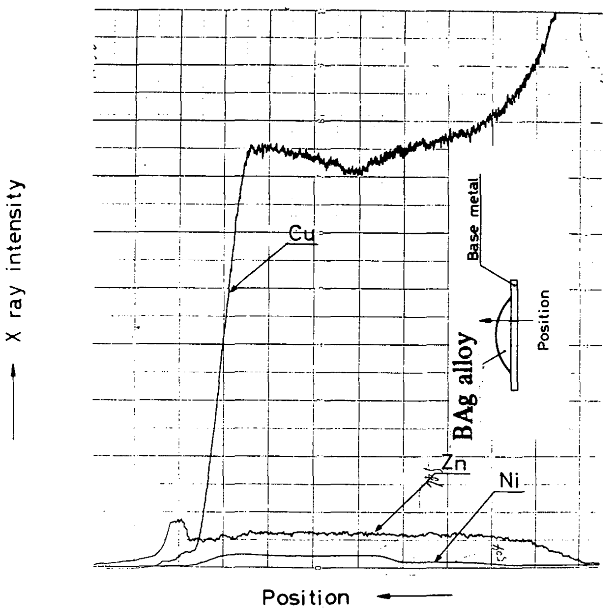


Fig. 5 Distribution of Ni in BAg-5 spread on Cu plate, using 10wt% $NiCl_2$ as flux

flux.

In Fig. 6 and Fig. 7, the results with 10wt%$SnCl_2$ are shown. From EPMA results, it is acknowledged that the dissolution amount of metal element from flux into BAg alloy is varied with the composition of flux and the variety of added metallic chlorides. Moreover, after spreading, the amount of Zn in BAg-1 is reduced in comparison with the one before, but the decrease of Cd in the alloy is not almost seen.

The phenomena may be due to the reaction(eq-4) between Zn in the alloy and metallic chloride in flux, because Zn may be the most base among Cd, Ag, Cu and Zn metals in BAg-1 alloy.

$$Zn\text{-}(BAg\text{-}1) + MCl_2 \xrightarrow{\triangle} ZnCl_2 + M\text{-}(BAg\text{-}1) \quad \text{- - - -} (4)$$

Namely, Zn reacts with metallic chloride, whose metal constituent is more noble than Zn, to give $ZnCl_2$. It is considered that Zn in BAg-1 alloy diminishes by the reaction. The reaction of various metallic chlorides with BAg alloy is explained in detail in next section.

As previously mentioned, the reaction of metallic chloride with Zn and the dissolution of metal from flux may be one of the main factor of improvement of brazability.

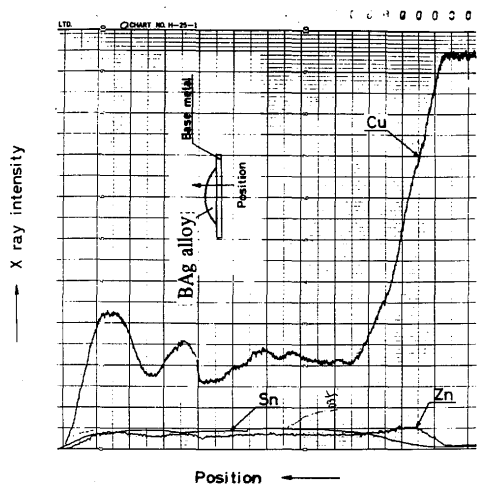


Fig. 6 Distribution of Sn in BAg-1 spread on Cu plate, using 10wt% $SnCl_2$ as flux

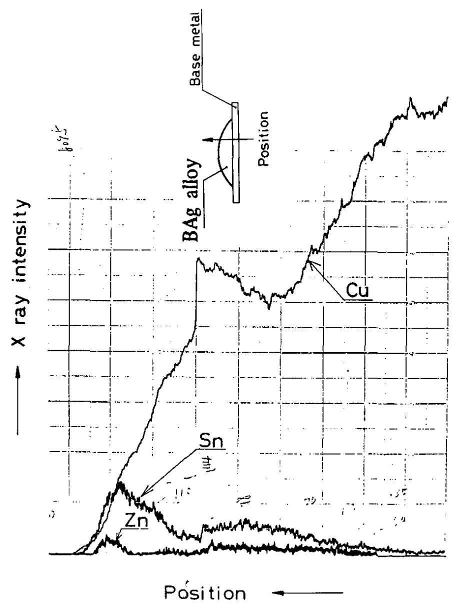


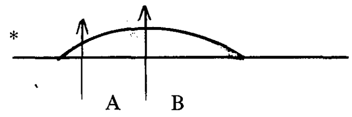
Fig. 7 Distribution of Sn in BAg-5 spread on Cu plate, using 10wt% $SnCl_2$ as flux

The difference of flux action between BAg-1 and BAg-5 is remarkable, when $FeCl_3$ is used as flux. The cause may be due to heating temperature, because spreading of BAg-1 at 800°C shows same degree as that of BAg-5 at 800°C.

The influence of concentration of metallic chloride in flux on dissolution of metal element from flux is shown in Tables 5 and 6 respectively, for $SnCl_2$ and $NiCl_2$. As expected, the dissolution amount of Sn or Ni increases with the increase of the amount of metallic chloride in flux, thus the spreading becomes better.

Table 5 Dissolution amount of metal containing in flux into BAg-5 spread on Cu plate

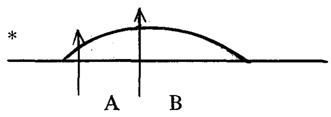
Flux	Analyzed position*	Dissolution amount**of metal from flux (%)
10 wt% $NiCl_2$	A	7
	B	3 (uniformly)
5 wt% $NiCl_2$	A	7
	B	3 (uniformly)
1 wt% $NiCl_2$	A	3
	B	2 (uniformly)



** relative x-ray intensity ratio by EPMA

Table 6 Dissolution amount of metal containing in flux into BAg-5 spread on Cu plate

Flux	Analyzed position*	Dissolution amount of metal from flux (%)**
10 wt% SnCl	A	7
	B	4 (uniformly)
5 wt% $SnCl_2$	A	4
	B	1 (uniformly)
1 wt% $SnCl_2$	A	2
	B	1 (uniformly)



** relative x-ray intensity ratio by EPMA

However, spread is disturbed by the precipitation of excess Ni on the surface or at the edge of spread alloy, when the concentration of $NiCl_2$ in flux becomes higher.

From above results, the difference in spreading between BAg-1 and BAg-5 on Cu plate was not almost seen, when various metallic chlorides were used as flux. Moreover, the effect of metallic chlorides on spreading may be depend mainly on the dissolution amount of metal element from chloride in these alloys, namely, on the reactivity between these alloys and metallic chloride.

Flux action of metallic chloride in brazing on Fe plate was studied as well in order to know precisely the effect of base metal. The result of spreading on Fe plate (armco iron) are shown in Fig. 8 and Fig. 9, respectively, for BAg-1 and BAg-5. In comparison with the results on Cu plate, $CoCl_2$, $CuCl_2$ and CuCl showed better effect especially on Fe plate. However, $FeCl_3$ which enhanced great spreading on Cu plate was not almost effective on Fe plate.

In order to know the relation between spreading and dissolution the cross section of the spreading

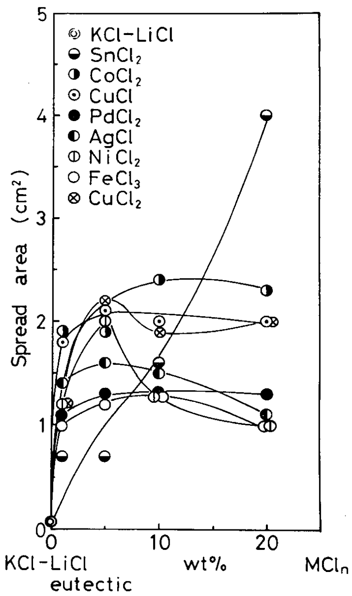


Fig. 8 Spread area of BAg-1 on Fe plate at 700°C for 1 min. vs. used flux composition

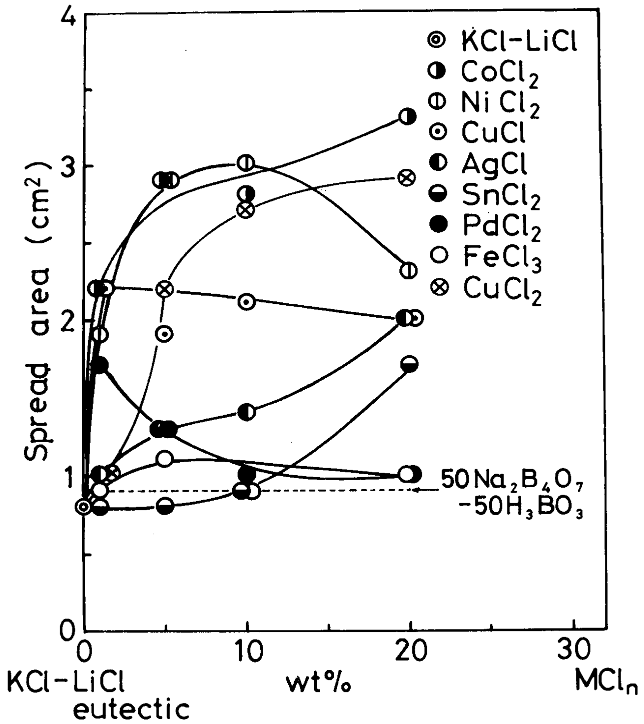
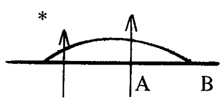


Fig. 9 Spread area of BAg-5 on Fe plate at 800°C for 1 min. vs. used flux composition

Table 7 Dissolution amount of metal containing in flux into BAg-1 spread on Fe plate

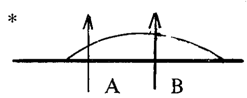
Flux	Analyzed position*	Dissolution amount** of metal from flux (%)
10 wt% $CoCl_2$	A	33
	B	20 (at surface) 24 (at interface)
10 wt% $SnCl_2$	A	13
	B	1 (uniformly)
10 wt% $FeCl_3$	A	4
	B	2
10 wt% $NiCl_2$	A	4
	B	10 (uniformly)
10 wt% $PdCl_2$	A	5
	B	8 (uniformly)



** relative x-ray intensity ratio by EPMA

Table 8 Dissolution amount of metal containing in flux into BAg-5 spread on Fe plate

Flux	Analyzed position*	Dissolution amount** of metal from flux (%)
10 wt% $NiCl_2$	A	5
	B	1 (uniformly)
10 wt% $CoCl_2$	A	29
	B	26 5 (at random) 3
10 wt% $PdCl_2$	A	8
	B	4 (uniformly)
10 wt% $SnCl_2$	A	10
	B	trace amount
10 wt% $FeCl_3$	A	trace amount
	B	trace amount



** relative x-ray intensity ratio by EPMA

specimens was analyzed by EPMA and the results were shown in Tables 7 and 8, respectively, for BAg-1 and BAg-5. X-ray micro analysis of Co and Zn was shown in Fig. 10 in the case of spreading with 10wt% $CoCl_2$ flux and BAg-5 alloy.

As shown in Fig. 10, a great amount of Co metal existed at the interface between base metal and deposited BAg-5 alloy. The phenomenon may contribute to improvement of spreading on Fe plate when $CoCl_2$ is used as flux. When metallic chloride takes marked effect on improvement of spreading, it is seen that metal from metallic chloride dissolves well in BAg alloy on Fe plate as well. So, it may be considered that the reaction between BAg alloy and metallic chloride is one of the important factors for the increase of spreading on Fe plate as well.

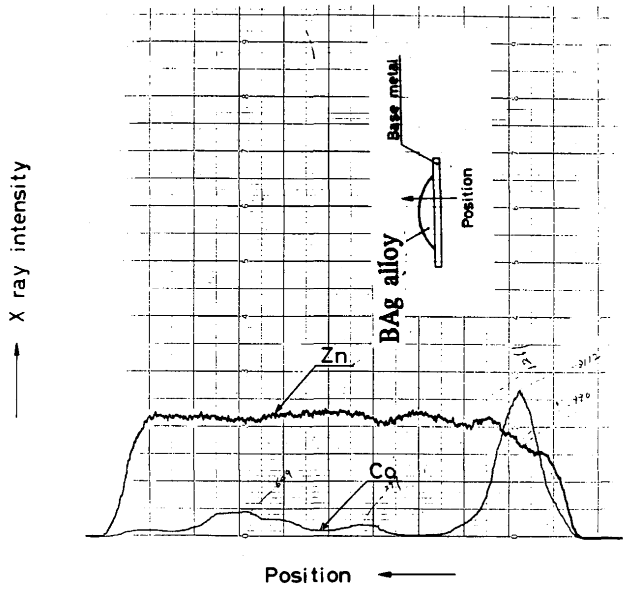


Fig. 10 Distribution of Co in BAg-5 spread on Fe plate using 10wt% $CoCl_2$ as flux

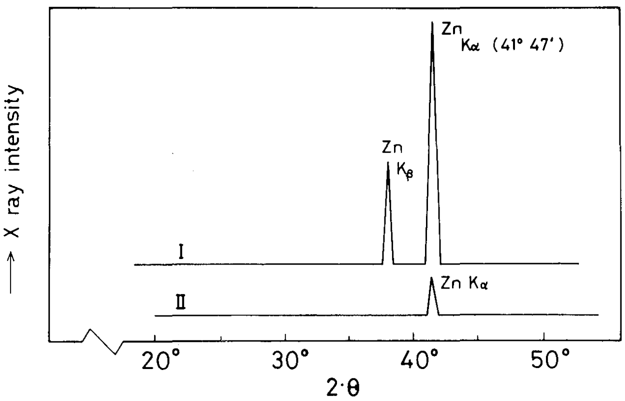


Fig. 11 Line profiles by fluorecent x-ray analysis
I) after reaction between BAg-1 and 90% KCl/LiCl eutectic 10% $CoCl_2$
II) after reaction between BAg-1 and KCl/LiCl eutectic

3.2 Factors controlling spread in this experiment

As mentioned in previous section, it was anticipated from the results analyzed by EPMA that Zn metal existing in BAg alloy might react with metallic chloride and the reaction was one of the important factors for the increase of spreading. To confirm the occurrence of the reaction, in the first place, the reaction of $CoCl_2$ with BAg-1 or BAg-5 was investigated qualitatively in molten KCL-LiCl eutectic salt. BAg-1 alloy(2g) and 10wt%$CoCl_2$-90wt%KCl/LiCl eutectic(2g) were heated up to 700°C in crucible and maintained at 700°C for 10 min. After the reaction, metallic chloride salt was dissolved in 30cc dis. water, and the amount of metal in the aqueous solution was measured by fluorecent X-ray analysis.

Moreover, same reaction with BAg-5 was investigated. The result of analysis for BAg-1 was shown in Fig. 11, where also the result of the reaction between BAg-1 and straight KCl-LiCl was written. As shown in Fig. 11, a great amount of Zn was observed in molten salt after the reaction, when $CoCl_2$ was added to KCl-LiCl eutectic. Similar results were obtained by the reaction of BAg-5 with $CoCl_2$. However, BAg alloy reacted poor with molten KCl-LiCl eutectic straight.

From above result, the fact was certified that $CoCl_2$ added to KCl-LiCl eutectic reacted with Zn bearing in BAg-1 or BAg-5 to give $ZnCl_2$, which dissolved in molten KCl-LiCl eutectic, as shown in eq-5 or eq-6.

$$CoCl_2 + Zn\text{-(BAg-1)} \xrightarrow{\triangle} ZnCl_2 + Co\text{-(BAg-1)} \quad \text{- - - (5)}$$

$$CoCl_2 + Zn\text{-(BAg-5)} \xrightarrow{\triangle} ZnCl_2 + Co\text{-(BAg-5)} \quad \text{- - - (6)}$$

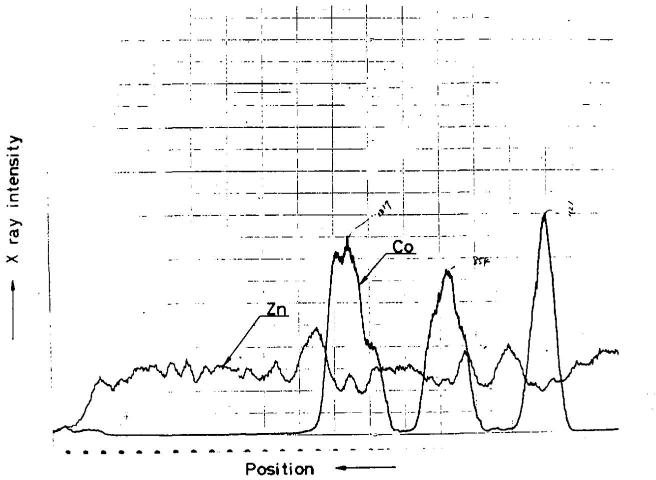


Fig. 12 Distribution of Co into BAg-1 heated in molten, flux, LiCl/KCl eutectic-10wt% $CoCl_2$ system, at 700°C for 10 min.

The existence of Co metal dissolved in BAg-1 or BAg-5 was confirmed by EPMA. The result for BAg-1 is shown in Fig. 12.

Next, the reaction of Zn bearing in BAg-1 with various metallic chlorides were studied quantitatively by the above method. The amount of Zn contained in molten KCl-LiCl eutectic salt after reaction was obtained by measuring X-ray intensity of Kα line (2θ=41.47). The results are shown in Table 9. From the result, it was confirmed that the reaction with Zn occurred also in the case of other metallic chlorides. The dissolution of

Table 9 Weight loss of Zn in BAg-1 after spreading test

Flux	Metal amount in flux (mg)	Wt. loss(mg) of Zn in BAg-1 after reaction	Metal amount (mg) produced by reaction (A)*
10 wt% $CoCl_2$	91	50	45
10 wt% $NiCl_2$	91	51	46
10 wt% $CuCl_2$	94	41	40
10 wt% CuCl	128	38	74
10 wT% $FeCl_3$	65	46	26
10 wt% $SnCl_2$	125	38	69
10 wt% $PdCl_2$	120	37	60
10 wt% AgCl	150	33	109

$$* Zn + MCl_2 \xrightarrow{\Delta} ZnCl_2 + M \text{ ---------- (A)}$$

metal from flux in BAg-1 after reaction was checked by EPMA. The reactivity between Zn and each metal chloride is as follows;

⟵ large small ⟶

$NiCl_2$, $CoCl_2$, $FeCl_3$, $CuCl_2$, CuCl, $SnCl_2$, $PdCl_2$, AgCl

When the spreading was taken into consideration on the basis of the above reactivity, it was recognized that metallic chloride which reacts well with BAg alloy did not always show the improvement in spread. And, spreading depends greatly on the variety of base metal. Namely, $CoCl_2$ is effective to spreadability on Fe plate, but relatively poor on Cu plate, in spite of having the best reactivity. However, $NiCl_2$ reacts very well with BAg-1 alloy, moreover, is most effective to spreading on both Cu and Fe.

When one considers the effect of added metal on wetting in brazing, the formation of intermetallic compound and solid solution between base metal and the added metal are important factor[6] to promote wetting. So it is required to consider the occurrences for spreading in our experiments also.

Namely, whether or not metal element dissolved in BAg alloy from metallic chloride by the above reaction has mutual solubility with base metal, moreover, whether or not the both metals form intermetallic compound has to be checked. From the point of the view of affinity between two metals, the reaction of metal dissolved in BAg alloy from metallic chloride with base metal (Cu and Fe) was taken into consideration on the basis of Gibbs free energy (ΔG)[7] (see Table 10) of mixing between two metals.

Namely, it is well known that the affinity between two metls is stronger, when the value of ΔG is larger in minus sign. Moreover, the occurrence of intermetallics for sure means that dissimilar atoms attract each other more than similar ones. Thus, Co metal produced by the reaction with BAg alloy has strong affinity with Fe as shown in Table 10, so that $CoCl_2$ showed the marked effect on spreading on Fe plate. However, on Cu plate,

Table 10 Free energy of mixing on each system

System	ΔG (cal/gr-atom)	Temp (K°)
Cu-Ag	−1225	1400
Cu-Ni	− 665	973
Cu-Pd	−2960	1000
Cu-Fe	− 680	1825
Fe-Ni	−3250	1873
Fe-Co	−1780*	1153
Ag-Cd	−2690	1100
Cu-Zn	−3250	1100

* $\Delta\bar{G}$

$CoCl_2$ was not effective to spreading, since it may be considered that Co metal has less affinity with Cu metal than with Fe metal, although $CoCl_2$ reacts well with BAg alloy.

On the other hand, the spreading on both plates was promoted largely by the addition of $NiCl_2$ to LiCl-KCl eutectic, as it is shown not only that Ni has a strong affinity with both Fe and Cu, but also that $NiCl_2$ reacts greatly with BAg alloy. The increase of spreading was realized by similar effect, when $PdCl_2$ was used as flux on Cu plate, although the reactivity of $PdCl_2$ with BAg alloy is the least.

The promotion of spreading on Cu plate by $FeCl_3$, and on Fe plate by $CuCl_2$ was observed by the strong affinity between Fe and Cu. However, other actions as corrosion of base metal and the elimination of oxide film on base metal, etc. may be effective to spreading.

From above results, the factor controlling wet or spread, may be dependent not only on the reactivity between metallic chloride and BAg alloy, but also on the affinity between base metal and metal which produced by the above reaction and was dissolved in BAg alloy. Namely, wetting or spreading can be improved by adding of metallic chloride to LiCl-KCl eutectic, which reacts well with molten BAg alloy, and of which metal has a comparably strong affinity with base metal.

4. Conslusion

The flux action of metallic chloride on brazing was investigated by relating between spreadability with BAg-1 or BAg-5 alloy. Moreover, spreading was considered on the basis of the afifnity between base metal and metal element of metallic chloride.

From the results, not only the reactivity, but also the affinity play a very important part in spreading or wetting on Cu or Fe plate. The reaction between metallic chloride and BAg-1 or BAg-5 takes place as follows,

$$\text{Zn-(BAg-1 or BAg-5)} + MCl_2 \xrightarrow{\Delta} ZnCl_2 + \text{M-(BAg-1 or BAg-5)}$$

M ; Ni, Co, Cu etc.

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