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# Studies on Brazability of Electric Contact Chip Materials (Report I)<sup>†</sup>

## — Effect of Surface Preparation of Sintered Tungsten Alloys on Wetting of BAg Filler Metals —

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### Abstract

*Effect of surface preparation of sintered tungsten alloys on wetting of BAg alloys was studied. The etching treatment with molten  $\text{NaNO}_2$  improved greatly the spreadability of filler alloys by making the surface rich in silver or copper due to the selective corrosion of tungsten in sintered alloys. Moreover, the better spreadability was gained by adding nickel or cobalt to filler alloys or sintered alloys. Then, the spread of filler alloys on sintered tungsten alloys was increased greatly due to nickel or cobalt coated on the surface of sintered alloys, when a flux containing  $\text{NiCl}_2$  or  $\text{CoCl}_2$  was used.*

### 1. Introduction

The contact chip for power circuit breaker is obtained by joining a sintered alloy to a heat-treated copper alloy with silver brazing. Silver-tungsten and copper-tungsten alloys are available as the sintered alloy, and harden copper, copper-chromium, copper-nickel-silicon etc. are used as the heat-treated copper alloy. However, a refractory tungsten oxide film forms on the surface of sintered alloy during brazing<sup>1)</sup>, and causes non-wetting and a poor joint, because a flux does not remove perfectly the oxide film. Then it appears that the tungsten contained in sintered alloy effects greatly on brazability. Therefore, various surface treatment methods were done to improve wetting for sintered tungsten alloys. In this experiment, two methods were studied as follows;

- 1) The first method which only tungsten on the surface of sintered alloys is dissolved by chemical etching before brazing, without to dissolve other remaining metals such as silver or copper on the surface<sup>2), 3)</sup>.
- 2) The second method using a flux containing metallic chloride of Co or Ni which forms a solid solution with tungsten.

Especially, this research was done to know the effect of these surface treatments of sintered alloys on spreadability of silver filler metal.

### 2. Experimental materials and methods

#### 2-1 Experimental materials

Such six kinds of sintered tungsten alloys as shown in Table 1 were used in this experiment as base metal. These specimens were polished with No. 320 emery paper and the dust and oil are eliminated by acetone before various tests. The used silver filler metals (dia.: 1.6 mm) also are shown in the Table 1. Eleven kinds of fluxes designated in Table 2 were used. These fluxes are composed mainly of  $\text{KF} \cdot 2\text{H}_2\text{O}$  and  $\text{KBF}_4$ .

Table 1 Nominal chemical compositions of brazing filler metals and base metals

		Chemical composition (wt %)						
		Ag	Cu	Sn	Zn	W	Co	Ni
Base metals	Ag-W	30	—	—	—	70	—	—
	Cu-W	—	30	—	—	70	—	—
	2.5Ni-Cu-W	—	Remain	—	—	70	—	2.5
	5.0Ni-Cu-W	—	Remain	—	—	70	—	5.0
	2.5Co-Cu-W	—	Remain	—	—	70	2.5	—
	5.0Co-Cu-W	—	Remain	—	—	70	5.0	—
Brazing filler metals	BAg-5	45	30	—	25	—	—	—
	BAg-4	40	30	—	28	—	—	2.0
	Silvaloy 254	40	30	—	25	—	—	5.0

<sup>†</sup> Received on October 29, 1977

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## 2-2 Pre-treatment of base metal before brazing

In order to improve the wettability of sintered tungsten alloy, we tried to eliminate only tungsten on the surface of sintered alloy by chemical etching before brazing, consequently the surface became richer in copper or silver.

As shown in Fig. 1, test specimen of sintered alloy

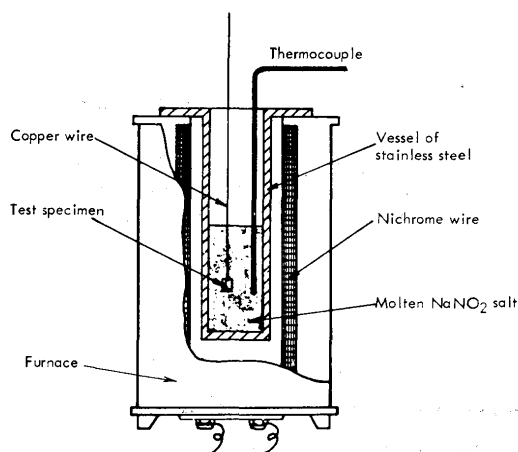


Fig. 1 Schematic view of apparatus for etching

(10×10×1 mm) was dipped in molten  $\text{NaNO}_2$  in a stainless steel vessel. The temperature of vessel was controlled by a thermo-couple dipped in  $\text{NaNO}_2$  and maintained at 280°C and 300°C for required time. The specimen was weighed before and after etching in molten  $\text{NaNO}_2$ . In order to observe the distribution of tungsten eliminated by  $\text{NaNO}_2$ , the surface of the specimen was analyzed by EPMA, together with other metal such as Ag or Cu. The analyzed position of specimen is shown in Fig. 2.

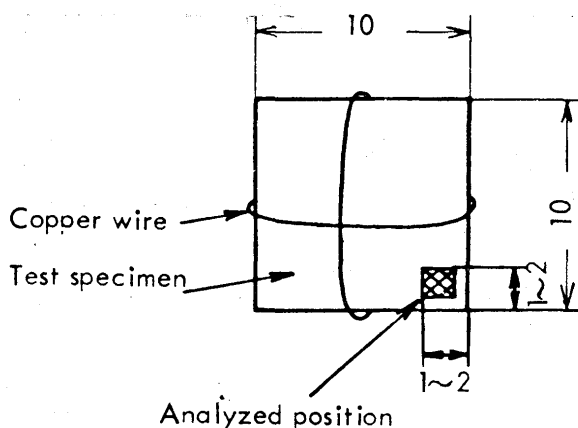


Fig. 2 Test specimen for etching in molten  $\text{NaNO}_2$  and position analyzed by EPMA

## 2-3 Spreading test method

The apparatus used for spreading test is shown in Fig. 3 and the tests were done as follows; BAg filler alloy wire (100 mg) was placed on the center of sintered alloy wholly fluxed, and then was heated at 800°C for BAg-5 and BAg-4 and 900°C for silvaloy 254, and kept at the temperature for 30 sec in an electric furnace. After finishing the spreading test, the area of spread BAg filler alloy was measured by a planimeter.

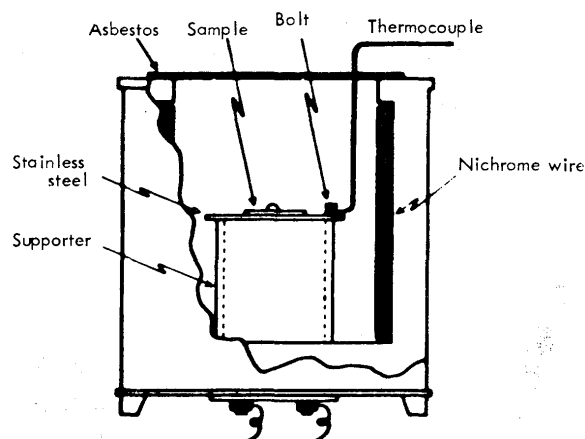


Fig. 3 Schematic view of apparatus for brazing test

## 3. Results and discussions

### 3-1 Etching of sintered tungsten alloy in molten $\text{NaNO}_2$

Photograph 1 shows the surface of Ag-W sintered alloy before etching. In the photograph, black parts

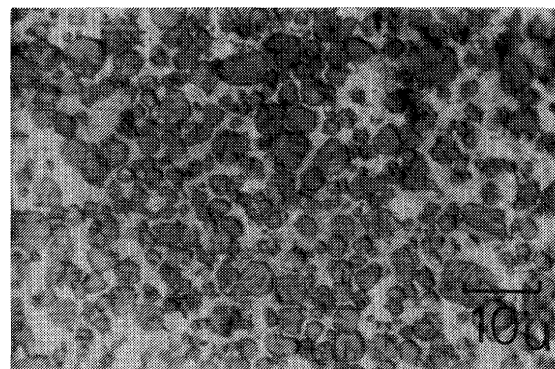


Photo. 1 Micrograph of surface of Ag-W alloy

show tungsten metal particle. This alloy was sintered by following method; tungsten powders are press-formed under some pressure and presintered at 1100°C. Then, the obtained tungsten skelton are dipped again in molten silver (or copper) at 1200°C for 1 hr. in a hydrogen atmosphere. However, tungsten hardly dissolves in molten silver, consequently, tungsten and

silver particles on the surface of sintered alloy exist independently, as shown in Fig. 4. The diameter of

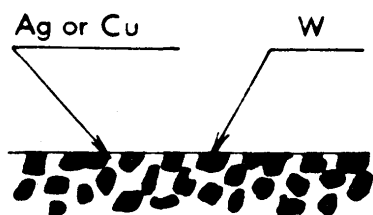


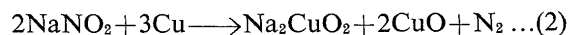
Fig. 4 Sectional view of sintered alloy

larger tungsten particle is about  $5\text{ }\mu\text{m}$ . As tungsten exposed to  $300\text{--}500^\circ\text{C}$  in air is oxidized rapidly and the formed tungsten oxides are tenacious, the brazability of sintered tungsten alloy decreases with increasing the content of tungsten in the sintered alloy. However, the better brazability is possible, if only tungsten and tungsten oxides on the surface are dissolved by chemical etching<sup>4)</sup>.

There are various conventional methods for etching of tungsten, such as etching in aqueous hydroxy alkali solution containing  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , electrolyte etching in 5% NaOH solution and etching in molten salt. As the etching rate in above aqueous solutions is very slow and is about  $50\text{ }\text{\AA}\text{--}350\text{ }\text{\AA}/\text{sec}$ , we adopted the etching in molten  $\text{NaNO}_2$  solution, in which the etching rate is fast. The reaction of Ag-W or Cu-W alloy with molten  $\text{NaNO}_2$  was considered as follows; in the case of Ag-W alloy, tungsten reacts with molten  $\text{NaNO}_2$  as shown in eq-(1).



However, silver remains on the surface of the alloy without etching since silver is more noble than tungsten. Therefore, the surface of Ag-W alloy after etching may become richer in silver. In the case of Cu-W alloy, both the reaction of eq-(1) and the reaction of copper with molten  $\text{NaNO}_2$  as shown in eq-(2) may occur.



And, CuO produced by the reaction exists on the surface of Cu-W alloy. However, CuO does not react with  $\text{NaNO}_2$ , and only tungsten may be corroded. So, the surface rich in copper and copper oxide may be obtained. From the above considerations, the surface rich in copper or silver may be obtained after etching in molten  $\text{NaNO}_2$ , and the brazability of sintered alloy may be improved. To confirm the occurrence of etching, the etching test in molten  $\text{NaNO}_2$  as shown in section 2-2 was done at  $280^\circ\text{C}$  and  $300^\circ\text{C}$ . Fig. 5 shows the relation between weight loss of the Ag-W or Cu-W alloy specimens and

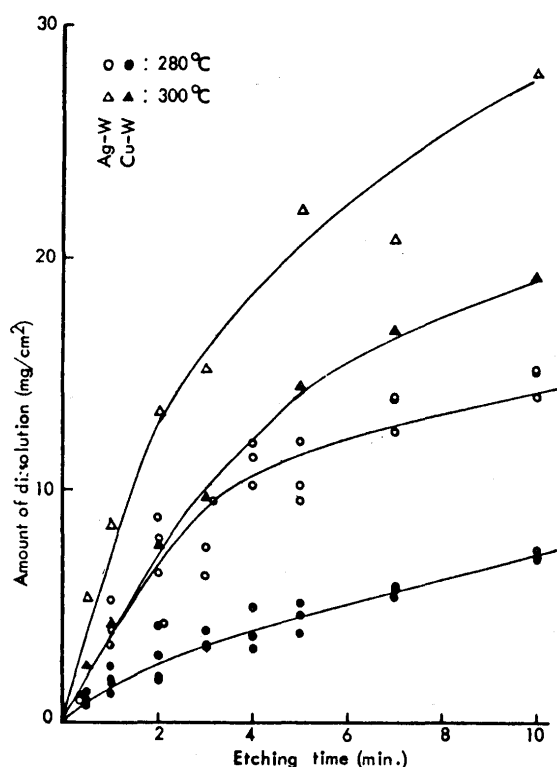


Fig. 5 Relation between amount of dissolution of W and etching time in molten  $\text{NaNO}_2$

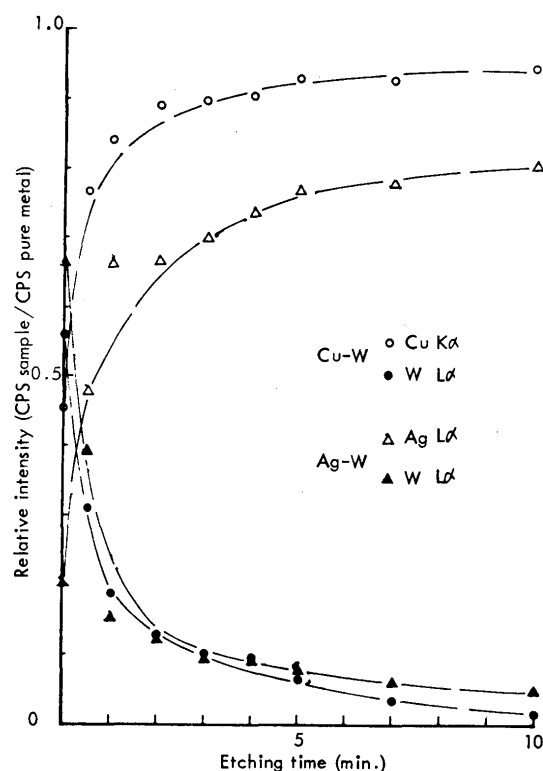
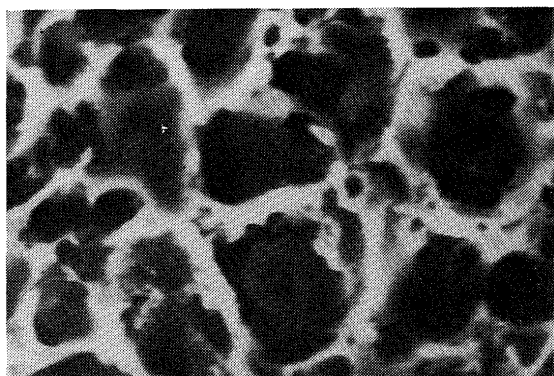


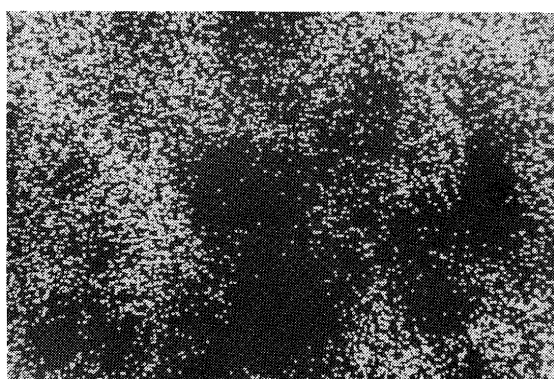
Fig. 6 Variation of surface compositions of sintered alloy dipped in molten  $\text{NaNO}_2$  at  $280^\circ\text{C}$

etching time. From the figure, the etching amount at  $300^\circ\text{C}$  is about 2 times as much as that at  $280^\circ\text{C}$ . Fig. 6 shows the relation between etching time and

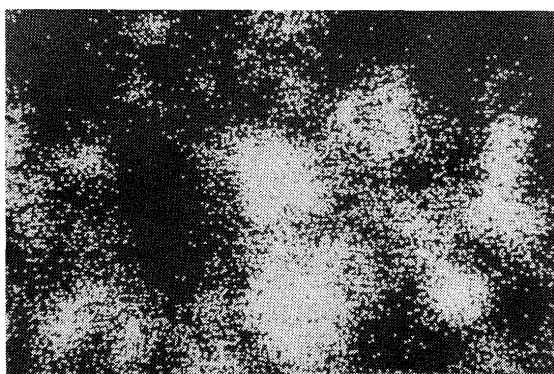
metal concentration ratio (relative X-ray intensity) on etched surface of sintered alloy in molten  $\text{NaNO}_2$  at  $280^\circ\text{C}$ . After etching for 3 min., the elimination of tungsten on the surface of sintered alloy was confirmed by EPMA and SEM. The analytical results are shown in **Photo. 2** for Ag-W alloy, and in **Photo. 3** for Cu-W alloy. From these photographs, the surface of both alloys after etching, in comparison with that before etching, is rich in silver or copper because of the dissolution of only tungsten by the above described reaction (eq-1).



(A)



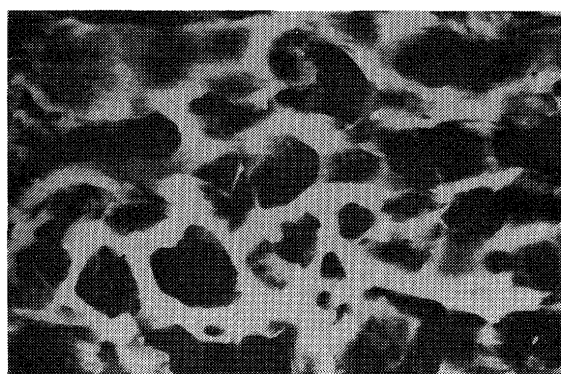
(B)



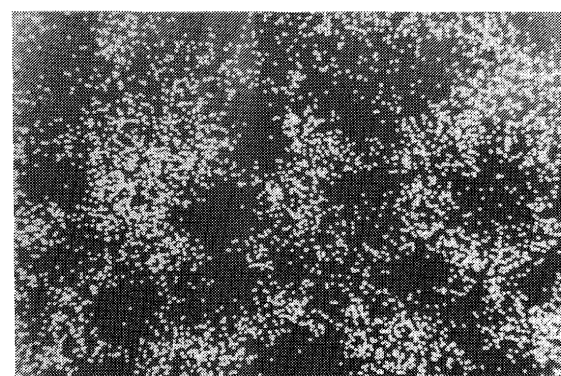
(C)

**Photo. 2** Surface of Ag-W sintered alloy etched in molten  $\text{NaNO}_2$  at  $280^\circ\text{C}$  for 3 min.

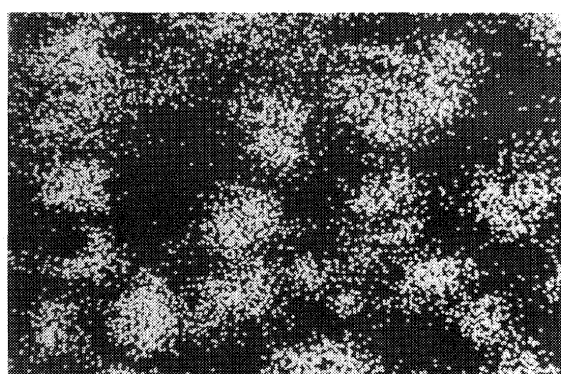
- A) Secondary electron image
- B) Characteristics X-ray image of  $\text{WLa}$
- C) Ibid. of  $\text{AgLa}$



(A)



(B)



(C)

**Photo. 3** Surface of Cu-W sintered alloy etched in molten  $\text{NaNO}_2$  at  $280^\circ\text{C}$  for 3 min.

- A) Secondary electron image
- B) Characteristics X-ray image of  $\text{WLa}$
- C) Ibid. of  $\text{CuK}\alpha$

### 3-2 Effect of etching treatment of sintered alloys on spreading of BAg filler metal

The wettability of the surface designated in Photos. 2 and 3 appears to be improved due to the preferential corrosion of tungsten, then, the spreadability of specimen etched in molten  $\text{NaNO}_2$  ( $280^\circ\text{C}$  for 3 min) was studied. Spreading tests were done at  $800^\circ\text{C}$  and  $900^\circ\text{C}$  with 0.1 g of BAg-5 or BAg-4 alloy and "A" type flux showed in Table 2. The results are shown in **Fig. 7**. From the figure, the spread area on each

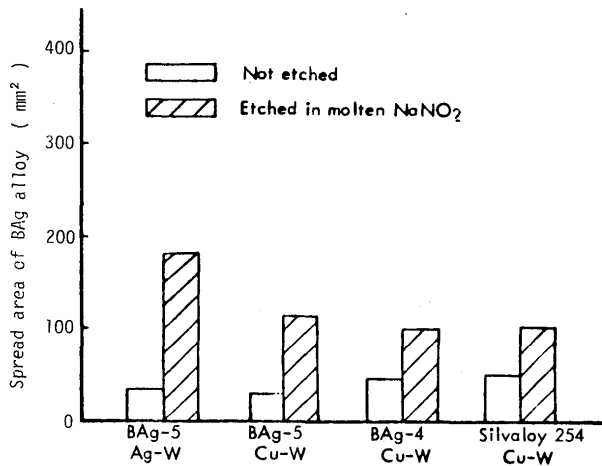


Fig. 7 Effect of etching in molten  $\text{NaNO}_2$  on spreading of brazing filler metals

surface of Ag-W and Cu-W alloy after etching is two times or more as large as that before etching. Both BAg-4 alloy and "silvaloy 254" alloys containing nickel gave two times larger spreading than BAg-5 alloy for non-etched sintered alloy. The addition of nickel to silver filler metal is believed to be effective for spreading on non-etched sintered alloy. However, the absolute value of spread area is less than that of the etched sintered alloy as shown in Fig. 7. From the above results, the etching in molten  $\text{NaNO}_2$  is superior to the addition of Ni to BAg filler metal for the brazing of sintered tungsten alloy.

### 3-3 Effect of addition of nickel or cobalt to sintered alloy on spreading of BAg filler alloy

In previous section, spreading area was increased by the elimination of tungsten metal on the surface of Cu-W sintered alloy. So, the spreading is con-

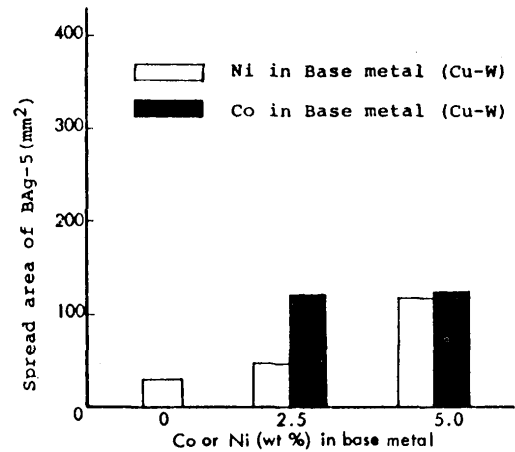


Fig. 8 Effect of addition of Co or Ni to base metal on spreading of BAg-5

sidered to be improved, when Cu-W sintered alloy containing Co or Ni as shown in Table 1 was used as base metal, because an amount of tungsten metal on the surface of the ternary sintered alloy is smaller than that on the surface of binary sintered alloy. The result of spreading test with "A" type flux and BAg-5 alloy is shown in Fig. 8. As shown in the figure, the addition of 5 wt% Co or Ni to Cu-W sintered alloy gave the same spread area as etching in molten  $\text{NaNO}_2$  did. However, the effect of addition of Co or Ni to Cu-W sintered alloy may can not be considered as same as the etching treatment in molten  $\text{NaNO}_2$ . The reason is as follows; as the sintered alloy is eliminated to about  $10\text{ }\mu\text{m}$  in depth by etching in molten  $\text{NaNO}_2$ , the surface is very rough and the molten filler metal penetrates into the rough surface. On the other hand, the surface is smooth in the case of Cu-W-Ni or Cu-W-Co ternary sintered alloy.

Table 2 Chemical compositions of fluoride system fluxes used

Flux	Compositions (wt %)		
	Main Substances $\text{KF} \cdot 2\text{H}_2\text{O}$ , $\text{KBF}_4$	Added metal chloride	Remains $\text{B}_2\text{O}_3$ , $\text{LiCl}$ , $\text{Na}_4\text{B}_{10}\text{O}_7$
A	○	—	○
C <sub>1</sub>	○	1.0 $\text{CoCl}_2$	○
C <sub>2</sub>	○	2.5 $\text{CoCl}_2$	○
C <sub>3</sub>	○	5.0 $\text{CoCl}_2$	○
C <sub>4</sub>	○	10.0 $\text{CoCl}_2$	○
C <sub>5</sub>	○	20.0 $\text{CoCl}_2$	○
N <sub>1</sub>	○	1.0 $\text{NiCl}_2$	○
N <sub>2</sub>	○	2.5 $\text{NiCl}_2$	○
N <sub>3</sub>	○	5.0 $\text{NiCl}_2$	○
N <sub>4</sub>	○	10.0 $\text{NiCl}_2$	○
N <sub>5</sub>	○	20.0 $\text{NiCl}_2$	○

### 3-4 Surface treatment by flux containing metallic chloride

#### 3-4-1 Effect of addition of $\text{CoCl}_2$ or $\text{NiCl}_2$ to "A" type flux on spreading

When Cu-W sintered alloy containing Co or Ni metal were used as base metal, the spreadability was improved greatly in comparison with that on Cu-W binary alloy. So,  $\text{CoCl}_2$  or  $\text{NiCl}_2$  was added to "A" type flux with variety of concentration as shown in Table 2, and the flux containing  $\text{CoCl}_2$  or  $\text{NiCl}_2$  was used in spreading test, in order to precipitate Co or Ni on the surface of Cu-W sintered alloy by the reaction between the base metal or the filler metal and  $\text{CoCl}_2$  or  $\text{NiCl}_2$  during brazing. Spreading tests were done with fluxes containing  $\text{CoCl}_2$  or  $\text{NiCl}_2$  on non-etched Cu-W sintered alloy. At  $800^\circ\text{C}$  for 30 sec, the result is shown in Fig. 9. The letters on each

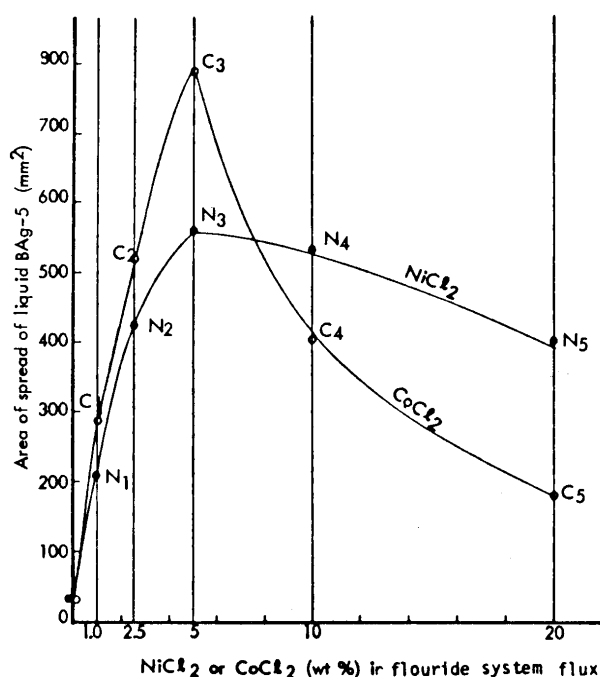


Fig. 9 Effect of addition of  $\text{CoCl}_2$  or  $\text{NiCl}_2$  to fluoride system flux on spreading of BAg-5

curve of this figure correspond to the letters of fluxes shown in Table 2. In the case of addition of 5 wt%  $\text{CoCl}_2$  or  $\text{NiCl}_2$ , the spread area shows max. value, and the spreadability is very much superior in comparison with that in the case of etching in  $\text{NaNO}_2$  or addition of Co or Ni to the base metal. So, the cross section of spread test specimens with 5 wt%  $\text{NiCl}_2$  flux was analyzed by EPMA, in order to know the concentration of Ni existing in the spread filler metal or the base metal. The result is shown in Fig. 10. It is found that Ni (about 5 wt%) is dissolved in the

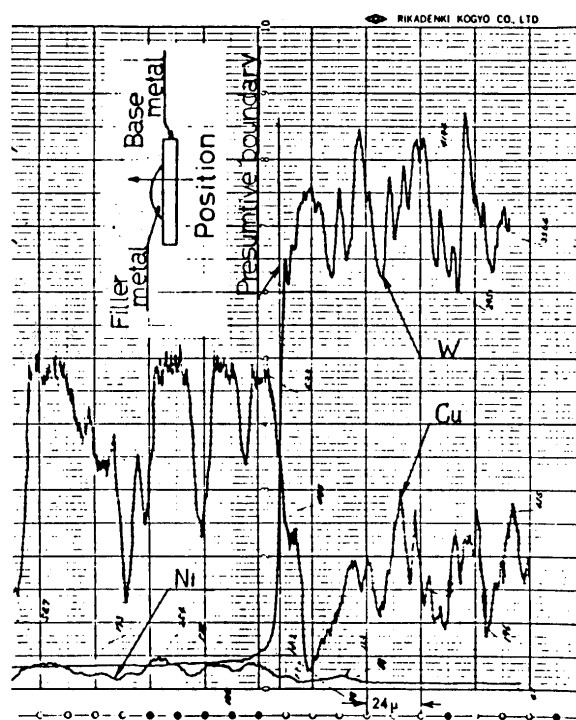


Fig. 10 Chart of EPMA of Cu, Ni and W for cross section of test specimen after spreading of BAg-5 on Cu-W sintered alloy with 5 wt%  $\text{NiCl}_2$ -fluoride system flux

spread filler metal and is less in the sintered base metal. From this fact, Co or Ni of the flux composition may contribute to the improvement of spreading.

#### 3-4-2 Effect of Co or Ni dissociated from flux on spreading

We note that the spreadability is improved by Co or Ni dissociated from the flux containing  $\text{CoCl}_2$  or  $\text{NiCl}_2$ . The cause may be considered to be due to the coating of Co or Ni on the surface of Cu-W sintered alloy. So, the surface of Cu-W sintered alloy was precoated by using the flux containing  $\text{CoCl}_2$  or  $\text{NiCl}_2$  as follows; the surface of Cu-W sintered alloy was wholly painted with the pasty flux and then was heated at  $800^\circ\text{C}$  for 1 min. After heating, the surface was washed with water and acetone and dried in air. BAg-5 alloy and "A" type flux were placed on the center of this precoated surface, in order to do the spreading test. The result was shown in Fig. 11. Spreadability increases to the same degree as that in the case of addition of 5 wt% Ni to Cu-W sintered alloy shown in Fig. 8. From the result analyzed by EPMA for the precoated surface of Cu-W sintered alloy (See Fig. 12), it is seen that about 5 wt% Ni exists on the surface. However, in the case of  $\text{CoCl}_2$ , the result shown in Fig. 8 is less in spreading than that in Fig. 11. Accordingly, the concentration of

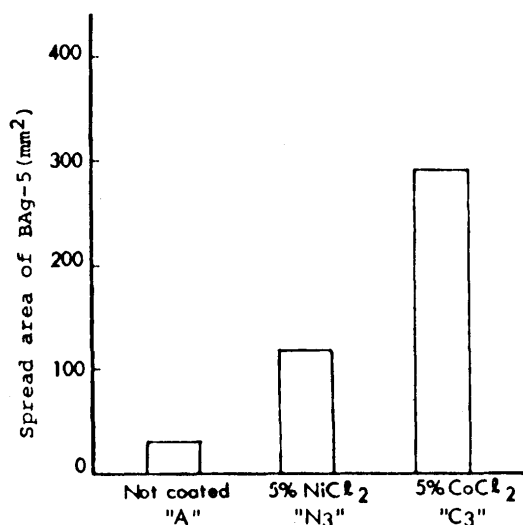


Fig. 11 Variation of spread area of BAg-5 on base metals of which surface were treated with fluxes "A", "C<sub>3</sub>" or "N<sub>3</sub>"

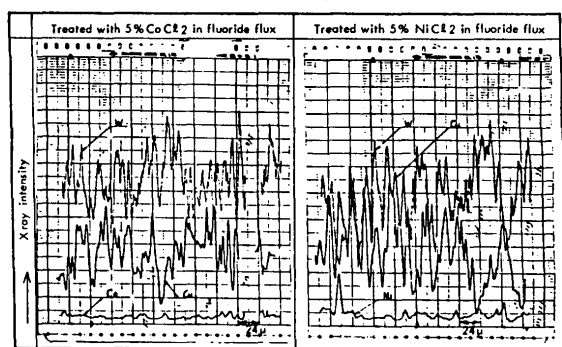


Fig. 12 Chart of EPMA of Co, Ni, Cu and W for surface of Cu-W sintered alloy treated with fluoride system flux containing 5% CoCl<sub>2</sub> or 5% NiCl<sub>2</sub>

metal precoated on the surface is not preferentially related to the spreadability, and the activated state of precoated metal dissolved by the used flux, which is "A" type flux, may also be considered to be important for the spreading (See Fig. 9, 5 wt% CoCl<sub>2</sub> in this case is added to "A" type flux).

#### 4. Conclusion

Surface preparation of sintered tungsten alloys (Ag-W, Cu-W alloy) was studied to improve the wetting of BAg alloy. Surface preparation was done by etching in molten NaNO<sub>2</sub>, adding cobalt or nickel to the filler metal or the sintered alloys, and using flux containing CoCl<sub>2</sub> or NiCl<sub>2</sub>. Several interesting results were obtained as follows:

- (1) The etching treatment of Ag-W or Cu-W sintered alloy in molten NaNO<sub>2</sub> made the surface rich in silver or copper by the selective elimination of tungsten. The spreadability of BAg filler metal on the etched sintered alloy was improved greatly in comparison with that on the non-etched sintered alloy.
- (2) The addition of cobalt or nickel to the silver filler metal or to the sintered alloys improved a little the spreadability with similar effect to the etching treatment.
- (3) By using the flux containing CoCl<sub>2</sub> or NiCl<sub>2</sub>, spreading of BAg-5 alloy on non-etched sintered alloy was increased greatly due to the coating of cobalt or nickel on the surface of sintered alloy.

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