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Spreading of BAg-5 on Pre-Flux Coated Stainless Steel Plate (Report II)†
— Function of Fluxes Mixed with CuCl or CoCl₂ —

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Abstract

The spreading mechanism of BAg-5 on the austenitic stainless steel surface, which was precoated and preheated with the specified fluxes before a spreading test, was considered from the observated results by SEM and by appling a concept of a surface roughness coefficient. On the other hand, the flux action of KCl-LiCl system for spreading of BAg-5 on pure metals such as copper, nickel, cobalt and iron plates was explained from a thermochemical consideration for the reducing reaction occurring between used flux and each base plate.

KEY WORDS: (Brazing) (Fluxes) (Halides) (Brazability) (Mechanism)

1. Introduction

Authers reported already[1] that a precoat-heated stainless steel plate with mixed salt fluxes, which were added $NiCl_2$ or $FeCl_3$ to KCl-LiCl system eutectic salt, showed a good property for spreading of BAg-5 using KCl-LiCl system eutectic salt flux.

In this paper, then, the specified fluxes that substituted $CuCl$ or $CoCl_2$ for $NiCl_2$ or $FeCl_3$ added to KCl-LiCl eutectic salt were used to know the effect for spreading of BAg-5. However, the experimental and considered results were similar to those of $NiCl_2$ or $FeCl_3$. For example, the spread area of BAg-5 on the stainless steel surface pretreated with the specified flux contained $CuCl$ was $\pi/2$ times the spread area that BAg-5 spread on a pure copper base plate using KCl-LiCl eutectic salt flux. And, this phenomenon has been also recognized for $NiCl_2$ as stated in previous paper[1]. From both facts, it was presumed that although copper differs nickel with physical and chemical properties, there is something in common with the spreading of BAg-5. Then, the spread area of BAg-5 on pure metals such as copper, nickel, cobalt and iron plates was investigated from the action of used flux. A flux, generally, removes a oxide film formed on base plate

in brazing and soldering. This fundamental flux action was introduced into a thermochemical analyzing procedure. The obtained result showed that the spread area of BAg-5 depended on the reducing power of used flux for the formed oxide film on the base plates and not depended on the wetting force of both each plate and BAg-5.

2. Experimental Apparatus and Procedures

Stainless steel plate (SUS304) was used as base plate for pre-flux coating, of which surface was polished by No.600 emery paper and degreased with acetone before pre-coating. Mixed salt fluxes added $CuCl$ or $CoCl_2$ to 54wt%KCl-LiCl eutectic salt flux were used to coat the plate surface of SUS304. The pre-coated plate surface was prepared as follows: the mixed salt, 2 gram, was applied at constant thickness to whole surface of base plate, which was heated at 800°C for 1 min. in an atmospheric and electric furnace. After holding of 1 min, the specimen was carefully removed to a cold copper plate to cool. The specimen, then, was washed in water and in acetone.

Observation for the surface and cross section of pre-

flux coating specimen and the spreading test of BAg-5 on the precoat-heated specimen were performed as same methods as stated in previous paper[1]. But, the spreading test on pure metal base plate was carried out as follows; the kind of used base plates and each purity are copper (JIS CuP-1), nickel (99.9%), cobalt (99.9%) and armco iron (C:0.013%, Si:0.02%, Mn:0.29%, P:0.025%, S:0.04%, Fe:Bal.). Those plates were sectioned by 40 x 40 x 0.5 mm and the surface was polished by No.600 emery paper and degreased with acetone. Then, KCl-LiCl eutectic salt flux, 0.2 g, and BAg-5 brazing filler metal, 0.1 g, were placed at the center on the surface of each base plate and heated at 800°C for 1 min. in an electric furnace in air. The spread area of filler metal was measured by a planimeter.

3. Results and Discussions

3.1 Effect of CuCl

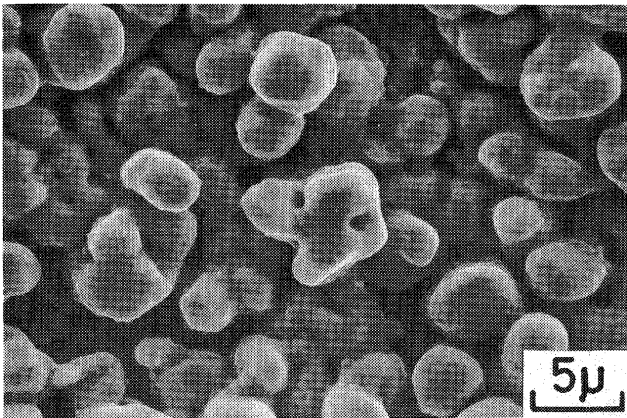**Photograph 1** shows the result of SEM analysis for the

Photo. 1 SEM microgragh of pre-coated surface with flux on 18Cr-8Ni stainless steel plate.
Conditions; flux, 10wt%CuCl and 90wt% eutectic salt of KCl-LiCl system, heating temp. and time, 800°C, 1min.

surface heated for 1 min. at 800°C after pre-coating with 10wt%CuCl-90wt%KCl-LiCl eutectic salt flux. As is visible in this photograph, the whole surface of base plate was covered with copper particles layer of mean particle diameter, 4.4 μm,. **Photo. 2** shows the result of SEM analyisis at cross section of the specimen shown in Photo. 1. Three layers such as (a), (b) and (c) are distinguished. The composition analysis of each layer by EDAX is shown in **Photo. 3**. The top layer (a) is copper alone and next layer (b) consists of copper and iron which contained in the base plate. And the chromium and the nickel elements contained in the base plate were not
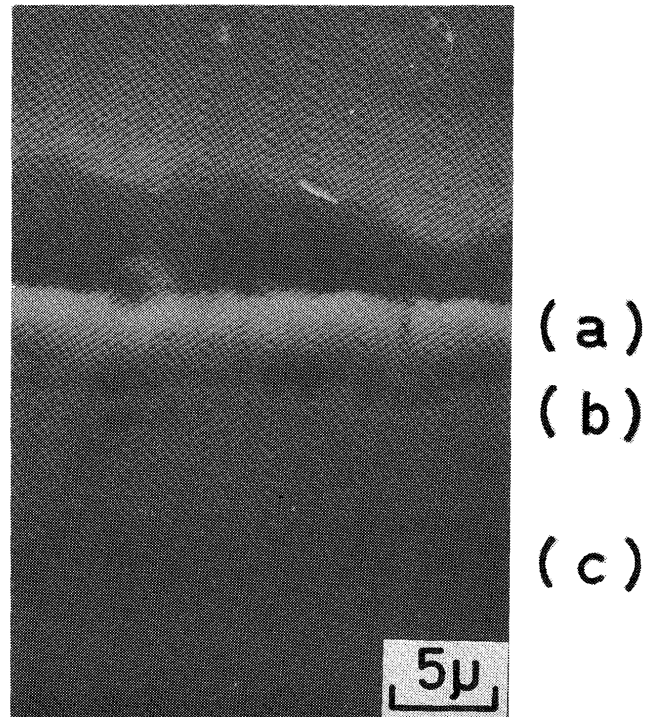

Photo. 2 SEM micrograph of cross section of same surface as Photo. 1.

detected in the second layer (b). The third layer (c) is identical with the chemical compositions of base plate. From these analysis results, it was considered that the chromium, the nickel and the iron contained in the base plate SUS304 dissolved into the molten salt and then Cu^{++} ion existing in the salt precipitated as many copper particles on the dissolved surface of base plate, because of an electrochemical reaction. This consideration was similar to the case of $NiCl_2$ described in previous paper[1].

3.2 Effect of CoCl₂

Photograph 4 shows the micrograph of SEM analysis for the surface heated for 1 min. at 800°C after pre-coating with 10wt%CoCl₂-90wt%KCl-LiCl eutectic salt flux. As is visible in the photograph, there is the scatter cobalt particles. **Photo. 5** shows the SEM analysis result at cross section of the specimen shown in Photo. 4. This section was also formed from three layers such as (a), (b) and (c). The composition of each layer by EDAX is shown in **Photo. 6**. The top layer (a) is cobalt and little iron, the second layer (b) consists of cobalt and iron. And the chromium, the nickel of base plate were not observed. Accordingly, this layer (b) appeared to be Co-Fe compound by applying same mechanism that $FeNi_3$ compound layer mentioned in previous paper[1] was formed on base plate. The third layer (c) is identical with the
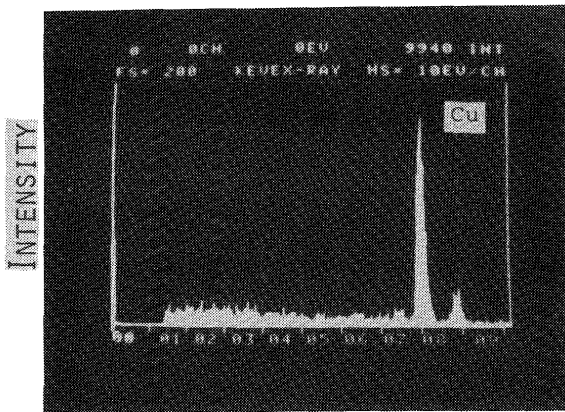
(a)
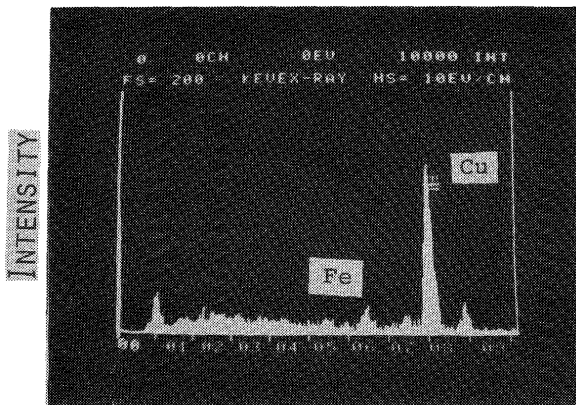
(b)
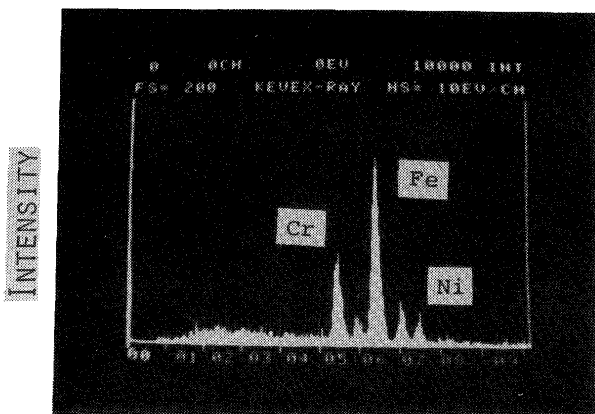
(c)

Photo. 3 EDAX results of each layer shown in Photo. 2; (a) Cu particles, (b) Cu-Fe compound, (c) 18Cr-8Ni stainless steel.
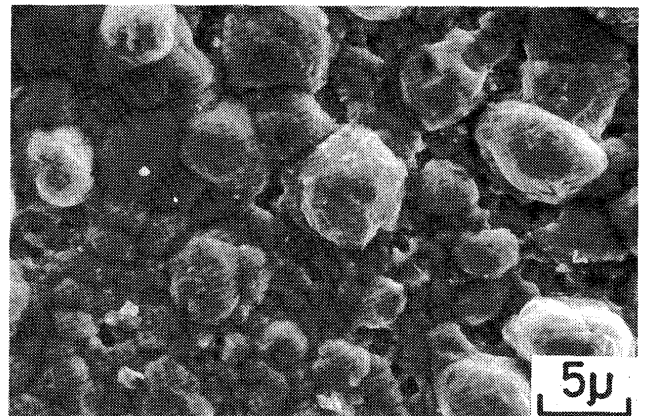

Photo. 4 SEM micrograph of pre-coated surface with flux on 18Cr-8Ni stainless steel plate.
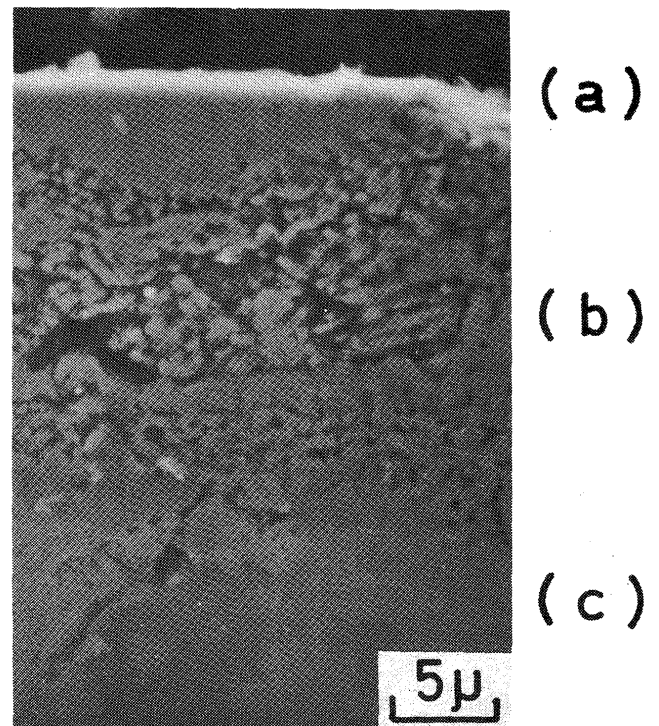Conditions; flux, 10wt%CoCl$_2$ and 90wt% eutectic salt of KCl-LiCl system, heating temp. and time, 800°C, 1 min.

(a)

(b)

(c)

Photo. 5 SEM microgragh of cross section of same surface as Photo. 4.

chemical compositions of base plate. As shown in photo. 5, however, the second layer (b) is very thick in comparison with the second layer (b) formed with 10wt%CuCl (See Photo. 2). Then, the folloing experiment was carried out to determine the weight loss of base plate dissolved by the molten each mixed fluxes. About 5g of the mixed flux were melted in a porcelain crucible inside a furnace mainted at 800°C. The base plate strip,

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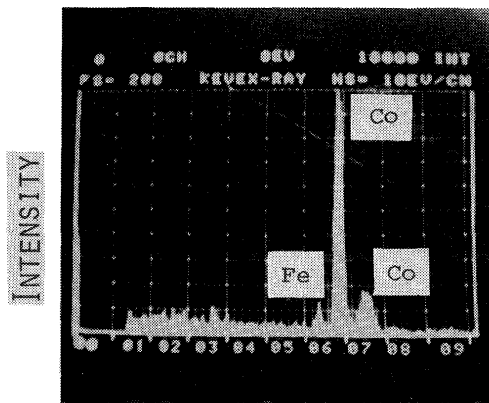
(a)
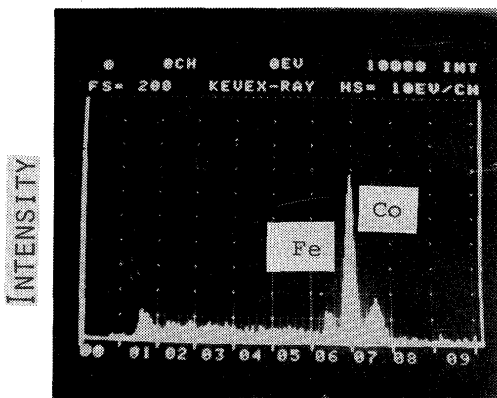
(b)

(c)

Photo. 6 EDAX results of each layer shown in Photo. 5; (a) Co particles, (b) Co-Fe compound, (c) 18Cr-8Ni stainless steel.

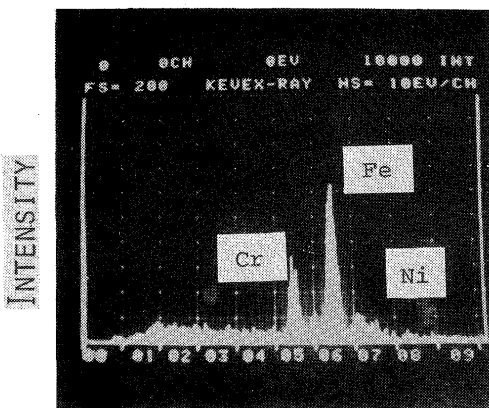SUS304, was weighed before dipping in the molten flux bath for the desired length of time. After dipping, the strip was removed from the molten flux bath, and washed in water and in acetone, dried and reweighed. The results of such weight loss determinations are shown in **Table 1.**

Table 1 Weight loss of base metal immersed in mixed salt fluxes at 800°C.

Flux \ Time(min.)	Weight loss of SUS 304(mg/mm^2)			
	1	2	3	5
KCl-LiCl eut.salt + 10wt% CuCl	2	2	3	3
KCl-LiCl eut.salt + 10wt% CoCl$_2$	7	15	22	40

The results show that only very small weight losses occur in the 10wt%CuCl flux, but much larger weight losses are obtained in the 10wt%CoCl$_2$ flux.

From this experimental fact and Photo. 5, the surface configuration shown in Photo. 4 is believed as follows; after the dissolution of chromium, iron and nickel from the surface of stainless steel plate into the molten flux has occured, the resultant surface becomes Co-Fe compound because of rapid alloying reaction between the precipitated cobalt particles and the iron contained in the base plate. On the other hand, the thickness of the second layer(b) shown in Photo. 2 is thiner than that of the second layer(b) shown in Photo. 5. The little weight loss of base plate dipped in the 10wt%CuCl flux as listed in Table 1 corresponds to the thin thickness of the former. From these facts, it was presumed that the copper particles of the top layer(a) shown in Photo. 2 act as a kind of passivated film, consequently, the dissolution of chromium and nickel contained in the base metal into the molten flux is prevented.

3.3 Spreading test

Figure 1 shows the results of spreading test made on each precoated and preheated surface discussed in previous paragraph, varing with the concentration of CuCl or CoCl$_2$ in the mixed fluxes. And the results of spreading
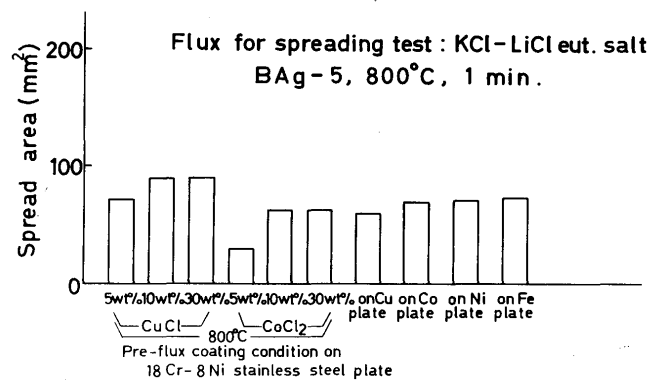

Fig. 1 Comparison of spreading test results.

test made on the pure metal plates are also shown in the figure.

As is visible in the figure, the spread areas on the specimens precoated and preheated with the mixed salt fluxes contained 5wt%CuCl or 5wt%CoCl₂ are less than those of 10wt%CuCl or CoCl₂, because the surface of the base plate is not covered fully with the precipitated metal particles such as copper or cobalt. However, the spread area becomes a constant value when the plate surface is covered perfectly as mentioned in previous paragraph, for instance, 10wt%-30wt%CuCl or $CoCl_2$. Furthermore, on the surface not precoated with each mixed salt flux, namely, on original base plate surface, BAg-5. filler metal could not quitely spread with the used test conditions. Next, the spread area on the specimen precoated and preheated with the mixed salt flux contained 10wt%CuCl is considered as follows: as shown in Photo. 1 the base plate surface was covered with copper particles layer. Then, as mentioned in previous paper[1], a concept of surface roughness coefficient is possible to apply for this consideration. If the copper particle is a sphere of 4.4 μm diameter and the arrangement of copper particles is simple cubic crystal structure, the total semi-spherical surface area of copper particles which exists on the most outside of copper layers shown in Photo. 1 is about $2\pi \times (2.2 \times 10^{-3})^2 \times 83 \times 10^6 = 2524$ mm². On the other hand, the surface area of smooth copper plate is 1600 mm², because of same size as stainless steel base plate. So, K value, the ratio of the total semi-spherical surface area of copper particles to the surface area of smooth copper plate, becomes about 1.57*. The spread area on the pure copper plate as shown in Fig. 1 is 60 mm² and K times of its value is 94 mm². As shown in Fig. 1, the spread area in 10wt%CuCl mixed salt flux is 90 mm². This experimental value agrees with the calculated value.

Next, the spread area on the base plate precoated and preheated with 10wt%CoCl₂ mixed salt flux is smaller than that of pure cobalt plate or pure iron plate. This difference can be attributed mainly to the fact that the Co-Fe compound layer as shown in Photo. 5 or Photo. 6 was formed on the base plate surface. And also, same phenomenon has been also observed in previous paper[1], namely, the spread area of BAg-5 on FeNi₃ compound layer was smaller than that of pure iron plate or pure nickel plate.

From these experimental facts, it was confirmed that additive property cannot to apply on the spread area of BAg-5 on the base plate of compound type such as Co-Fe or FeNi₃. Although Kawasaki[2][3] had reported that the spread area of tin-lead solder on Cu₃Sn (ϵ phase) or Cu₆Sn₅ (η phase) was improved, these compounds consist of tin of solder and the copper of base plate. Accordingly, it should be noted that the compounds in our experiment differ from the growthing process, namely, consist of the metal elements contained in mixed salt fluxes and the iron of base plate.

3.4 Spread area of BAg-5 on pure metal base plates

In this paragraph, the flux function of KCl-LiCl system eutectic salt related with the spread area of BAg-5 on pure metals such as copper, cobalt, nickel and iron plates was considered by using a thermochemical analyzing procedure. It is well known generally that a fundamental flux action is to remove a oxide film formed on a base plate during and before brazing. So that, following reaction is assumed in our experiment.

$$MO + 2LiCl \longrightarrow MCl_2 + Li_2O + q \qquad (1)$$
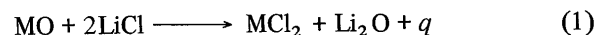
where M is metal elements such as Cu, Co, Ni and Fe, q is the heat of reaction. Because KCl-LiCl eutectic salt flux was used in this experiment, the equation replaced KCl with LiCl of equation (1) may be necessary. However, when such equation was used on the consideration described below, the tendency of obtained results agreed with that of equation (1). Therefore, only the data for equation (1) have been described in following thermochemical analysis.

Table 2 Formation heat of relevant oxides, chlorides and q values of eq(1).

Base plates	Oxides MO(K cal/mol)	Chlorides MCl_2 (K cal/mol)	q_{298}(Kcal/mol)	q_{1073}(Kcal/mol)
Cu	37.1 ± 0.8	49.2 ± 2.5	-47.4	-50.1
Co	57.1 ± 0.5	77.8 ± 4.0	-40.0	-43.0
Ni	57.5 ± 0.5	73.0 ± 0.5	-41.7	-41.3
Fe	63.2 ± 0.3	81.8 ± 0.2	-38.1	-40.7

* Calculated K value was also 1.57(=$\frac{\pi}{2}$) in previous paper[1]. On the assumption that precipitated particles are a sphere, K value of roughness factor is always 1.57 in spite of particle diameter.

The formation heat of each oxide and chloride at 298°K is listed in Table 2. These values, as shown in the

table, have a little of allowable value. Therefore, the reaction heat, q_{298}, of equation (1) was calculated with the maximum formation heat before reaction and the minimum formation heat after reaction, In this calculation, the formation heat of common component is LiCl =96.9 ± 2.0 and Li_2O=142.6 ± 1.0 Kcal/mol respectively. The obtained values are listed in Table 2 and these values denote the enough heat necessary to occur the reaction shown in equation (1). Moreover, the present spreading test was carried out at 1073°K (800°C), then, the reaction heat, q_{1073}, at a temperature was calculated with the temperature dependence equqtion of molar heat content of each oxide and chloride given by a literature[4] and Kirchhoff's law, and is listed in Table 2. From these values, it is possible to know that all reactions in the present work are endothermic reaction. So that, the relation between q_{1073} and the spread area is plotted in **Fig. 2**. As is visible in the figure, a liner relation was obtained. **Table 3** shows the calculated results of molar

Table 3   Molar surface area of relevant oxides.

	CuO	CoO	NiO	FeO
Molecular weight	79.5	74.9	74.7	71.8
Density(g/cm^3)	6.4	6.3	6.8	5.7
Molar surface area(cm^2)	5.4	5.2	4.9	5.4

surface area of each oxide. This result showed that the molar surface area of each oxide is equal approximately, although NiO, 4.9 cm^2, is slightly less than other three oxides. If this evaluation is correct, the liner relation obtained in Fig. 2 confirmed that the spread area of
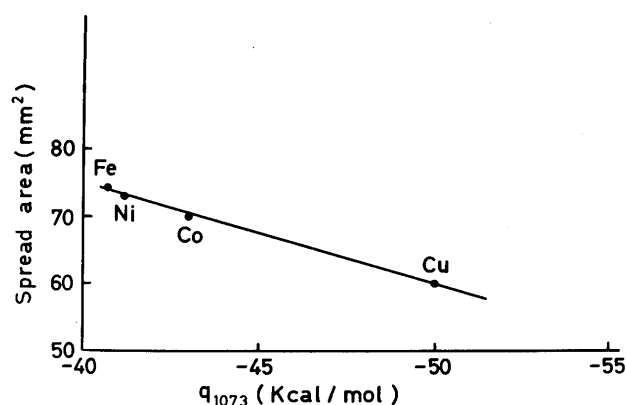

Fig. 2 Relation between spread area and reaction heat of eq(1).

BAg-5 on each pure metal plate decreases with the increasing of reaction heat necessary to remove the oxide film formed on each base plate with the used flux, KCl-LiCl eutectic salt.

From the above mentioned thermochemical considera-

tion, it was discovered under the present work conditions that the spread area of BAg-5 depended on the reducing power of used flux for the formed oxide film on the base plates and not depended on the wetting force of both each plate and BAg-5.

4. Conclusions

In this study, after a stainless steel plate pre-coated with the mixed salt flux was heated, corrosion products formed on the plate surface were analyzed by SEM and X ray diffractometer. On the other hand, a spreading test of Bag-5 on the same treated plate was carried out with KCl-LiCl eutectic salt flux. Moreover, the flux function of KCl-LiCl eutectic salt which affected the spread area of BAg-5 on pure metals such as copper, cobalt, nickel and armco iron plates was examined.

From these experiments, the function of used fluxes on spreading of BAg-5 was concluded as follows;

(1) At the interface between molten KCl-LiCl-CuCl system mixed salt and 18Cr-8Ni austenitic stainless steel plate, the chromium, the iron and the nickel dissolve from the stainless steel plate surface by electrochemical reaction, thus producing the covered surface with copper particles layer. This surface enlarges the spread area of BAg-5 with KCl-LiCl eutectic flux and its extent is $1.57(=\frac{\pi}{2})$ times that of BAg-5 on pure copper plate with same flux.

(2) At the interface between molten KCl-LiCl-CoCl$_2$ system mixed salt and 18Cr8Ni austenitic stainless steel plate, the chromium and nickel dissolve from the stainless steel plate surface by electrochemical reaction. The cobalt in the mixed salt precipitates on base plate and forms the compound, Co-Fe, with the iron in base plate. This surface is superior than the original surface of the base plate for spreading of BAg-5 with KCl-LiCl eutectic flux, but is inferior than the pure cobalt or iron plate surfaces.

(3) It was discovered that the spread area of BAg-5 on pure metals such as copper, cobalt, nickel and armco iron plates with KCl-LiCl eutectic flux depended on the reducing power of used flux for the formed oxide films such as CuO, CoO, NiO and FeO on base plates, whereas not depended on the wetting force of both each plate and BAg-5.

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