Spreading of BAg-5 on Pre-Flux Coated Stainless Steel Plate†

– Function of Fluxes Mixed with $NiCl_2$ or $FeCl_3$ –

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Abstract

The flux function of $NiCl_2$ or $FeCl_3$ on spreading of BAg-5 filler metal on SUS304 stainless steel plate was studied. When the pre-coated stainless steel surface with flux containing $NiCl_2$ was heated, nickel particle layer was formed on $FeNi_3$ compound layer given by dissolution of chromium and iron from stainless steel surface. In the case of flux containing $FeCl_3$, only $FeNi_3$ compound layer was formed.

It was confirmed that these layers on stainless steel surface contributed to the improvement of spreading.

1. Introduction

Authors had reported already that the spreading of BAg-5 filler metal on mild and stainless steels could be improved by adding small amounts of $NiCl_2$ or $FeCl_3$ to KCl-LiCl eutectic salt flux.[1)2)3)] In this study, then, to know the flux function of $NiCl_2$ or $FeCl_3$, a 18Cr-8Ni stainless steel plate, SUS304, was pre-coated with the mixed salt flux and was heated for 1 min. of the same time as that in previous spreading test.[1)2)3)] The substances formed on this plate surface were nickel particle and $FeNi_3$ compound layers for the mixed flux containing $NiCl_2$, and $FeNi_3$ compound layer for the $FeCl_3$ mixed flux. The appearance of these layers showed that the plate surface was corroded in the mixed salt flux and the nickel particle precipitated on the $FeNi_3$ compound layer by electrochemical reaction. Furthermore, it is an interesting fact that the chromium of chemical compositions of 18Cr-8Ni stainless steel is not seen in these layers. A chromium oxide film disturbes the spreading of filler metal. Therefore, a spreading test of BAg-5 filler metal on these layers was made by using KCl-LiCl eutectic salt flux, excepting $NiCl_2$ or $FeCl_3$.

The result obtained in this experiment showed that "De-chromiumnization" phenomenon on the surface of stainless steel may be one of the important function of flux used.

2. Experimetal Apparatus and Procedures

Stainless steel plate (SUS304, 40x40x0.5mm) was used as base metal, of which surface was polished by No. 600 emery paper and degreased with acetone before precoating. Mixed salt fluxes added $NiCl_2$ or $FeCl_3$ to 54wt%KCl-LiCl eutectic salt were used to coat the plate surface of SUS304. The pre-coated plate surface was prepared as follows: The mixed flux, 2 gram, was applied at constant thickness to whole plate surface of base metal, which was heated at required temperature for 1 min. in an atmospheric electric furnace. After cooling to room temperature, the specimen was washed with water and acetone.

Spreading test was done with the KCl-LiCl eutectic salt, 0.2 gram, and BAg-5 brazing filler metal, 0.1 gram. The filler metal and eutectic salt flux were placed at the center on the pre-coated and heated plate surface and the specimen was re-heated at 800°C for 1 min. by using the apparatus shown in previous paper[4)]. The spread area of filler metal was measured by a planimeter.

For the observation of the surface and cross section of the heated specimen, SEM or X-ray diffractometer (CoKα, Fe filter; 35Kv, 10mA) was used. Furthermore, energy dispersive X-ray analysis system (EDAX) attached to the SEM was used to quantitatively identify the element on the plate surface.

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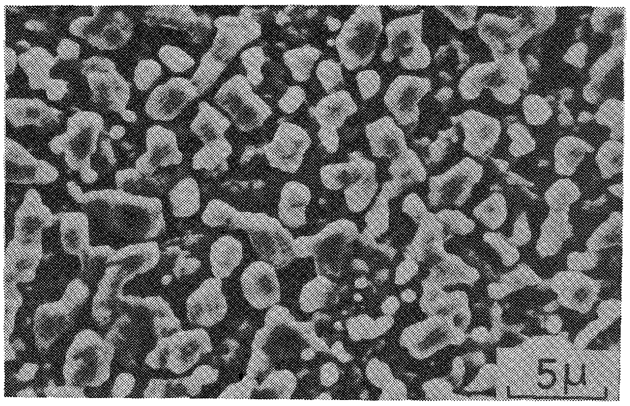

Photo. 1 SEM micrograph of pre-coated surface with flux on 18Cr-8Ni stainless steel plate.
Conditions: flux, 10wt%$NiCl_2$ and 90wt% eutectic salt of KC1-LiCl system, heating temp. and time, 500°C, 1 min.

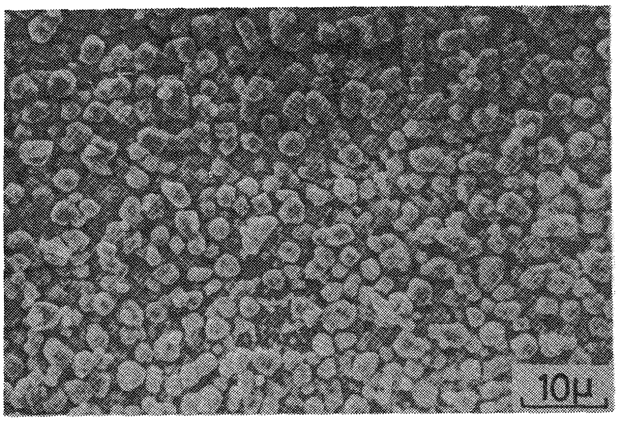

Photo. 2 SEM micrograph of same surface as Photo. 1 but temp. is 800°C.

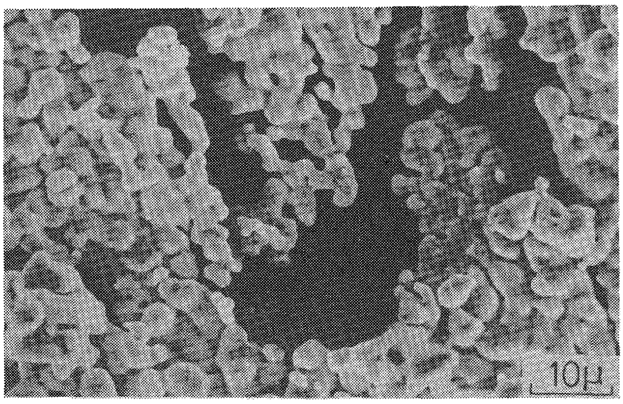

Photo. 3 SEM micrograph of same surface as Photo. 1 but temp. is 900°C.

3. Results and Discussions

3.1 Observation of pre-coated and heated SUS304 stainless steel plate

The results of SEM analysis were shown in **Photo.** 1, **Photo.** 2 and **Photo.** 3 for the surfaces heated for 1 min., respectively, at 500, 800 and 900°C after pre-coating with 10wt%$NiCl_2$-90wt%KCl-LiCl eutectic salt flux.

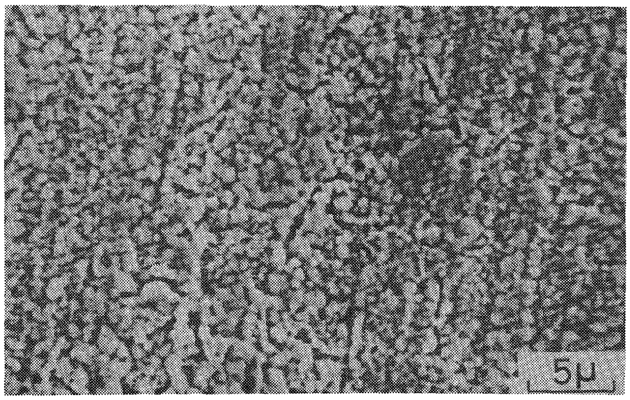

Photo. 4 SEM micrograph of pre-coated surface with eutectic salt of KCl-LiCl system on 18Cr-8Ni stainless steel plate, Conditions: 800°C, 1 min.

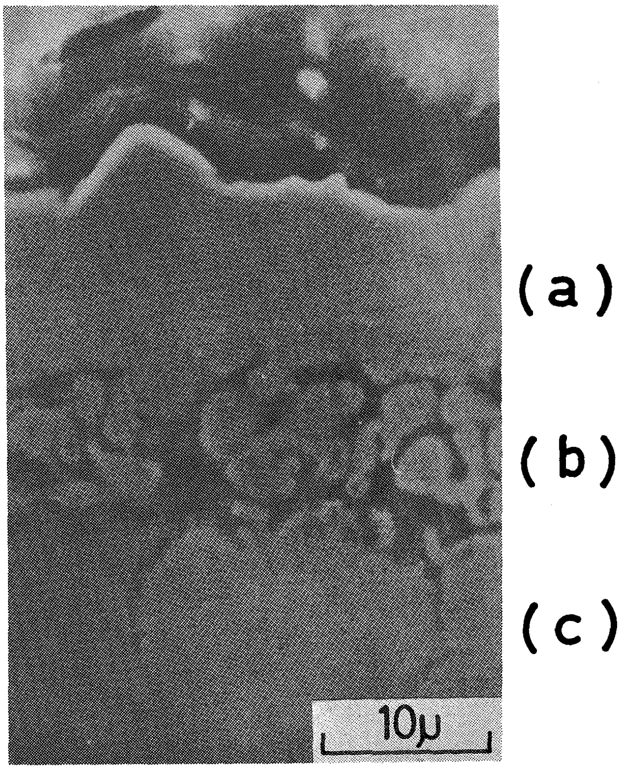

Photo. 5 SEM micrograph of cross section of same surface as Photo. 2 but flux is 30wt%$NiCl_2$.

From the results of SEM analysis, the increase of number of precipitated particles on the surface was seen with the raise of heat-temperature, when the flux added 10wt%$NiCl_2$ to KCl-LiCl eutectic salt was used for pre-coating. Then, these surfaces were detected by X-ray diffractometer. The original chemical compositions such as iron, chromium, nickel were observed on the surface heated at 500°C shown in Photo. 1, whereas were little $FeNi_3$ compound. However, nickel and $FeNi_3$ compound were detected on both surfaces shown in Photo. 2 and Photo. 3, respectively heated at 800 and 900°C, whereas chromium was not detected. **Photo.** 4 shows the surface pre-coated with KCl-LiCl eutectic salt only and heated for 1 min. at 800°C. The result of X-ray diffraction analysis on this surface showed plane chemical composition of base metal. To know more detail of the surface configuration, the amount of $NiCl_2$ was increased to 30wt% and heated for 1 min. at 800°C. **Photo.** 5 shows the result of SEM analysis for the specimen in cross section. Three layers such as (a), (b) and (c) are distinguished there. The composition analysis of each layer by EDAX is shown in **Photo.** 6. The top layer (a) is nickel alone and the second

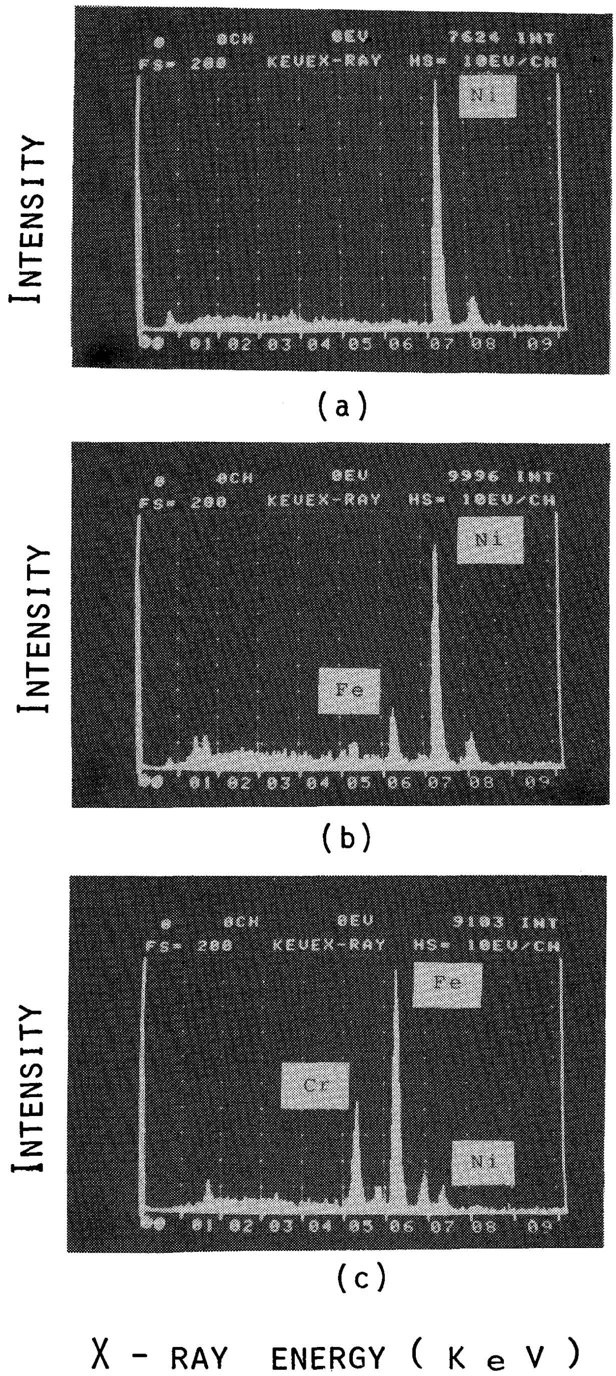

Photo. 6 EDAX results of each layer shown in Photo. 5: (a) Ni particles, (b) FeNi3 and Ni particles, (c) 18Cr-8Ni stainless steel.

layer (b) consists of nickel and iron, however the same colour parts as the top layer (a) were nickel alone. Accordingly, some dark parts in second layer (b) appeared to be $FeNi_3$ compound, judging from the X-ray diffraction analysis results mentioned above. The third layer (c) is identical with the chemical compositions of base plate.

From these analysis results, the number of particles observed in Photos. 2 and 3 were considered to be nickel and beneath $FeNi_3$ compound.

After the plate surface was pre-coated with 10wt%$FeCl_3$-90wt%KCl-LiCl eutectic salt and heated for 1 min. at 800°C, the surface was analyzed by SEM. The result is shown in **Photo.** 7. This surface configuration is

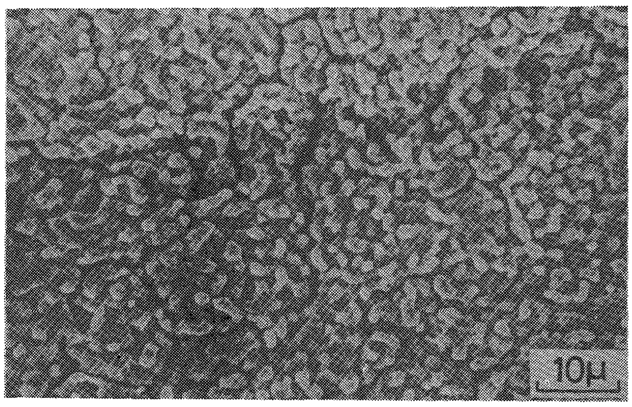

Photo. 7 SEM micrograph of pre-coated surface with flux on 18Cr-8Ni stainless steel plate. Conditions: flux, FeCl3 and 90wt% eutectic salt of KCl-LiCl system; heating temp. and time, 800°C, 1 min.

spongy. The X-ray diffraction analysis result of this surface showed $FeNi_3$ compound and no both nickel and chromium.

From above mentioned results, it was discovered that "Dechromiumnization" phenomenon on the surface of stainless steel occurred by corrosion reaction, when the mixed flux containing $NiCl_2$ or $FeCl_3$ was used for pre-coating.

Next, in order to confirm the formation process of both layer (a) and layer (b) in Photo. 5, we estimate the number of nickel atoms composing the layer (a) in Photo. 5 as follows;

The number of Ni^{++} ions existing in 30wt%$NiCl_2$-70wt%KCl-LiCl eutectic salt, 2 gram, is about 28.2×10^{20}, if $NiCl_2$ dissociates completely into ions in molten salt.

On the other hand, the number of nickel particles existing in about 10μm thick layer (a) is about 1.78×10^8 (number of nickel particles containing in monolayer of the layer (a))x3.33 (number of the monolayer)=5.93×10^8, if nickel particle is estimated as a sphere of mean 3μm diameter, and the arrangement of nickel particles is simple cubic crystal structure. Well each of nickel particles contains 1.29×10^{12} nickel atoms as a nickel is *fcc* crystal structure and a latice constant is 3.52Å. Accordingly, the total number of nickel atoms in the layer (a) become about 7.65×10^{20}. As nickel particles exist too in the layer (b) shown in Photo. 5 as described above, the amount of nickel atoms existing in both the layer (a) and layer (b) appears to be about 40-50 percent of the $NiCl_2$ added in the mixed flux. So it may be considered that these nickel particles in these layers are based on the precipitation from the mixed flux and the boundary* between the layer (a) and the layer (b) is original surface of stainless steel plate before pre-coating. Furthermore, the surface configuration shown in Photos. 2, 3 and 7 is believed as follows. After the dissolution of chromium and iron from the plate surface of stainless steel into the molten fluxes has occured, the resultant surface becomes spongy $FeNi_3$ compound as shown in Photo. 7. If, a mixed flux contains a noble metal than chromium and iron, such as nickel, the nickel particle layer on spongy $FeNi_3$ compound layer forms.

3.2 Spreading Test

Figure 1 shows the results of spreading test made on each surface discussed in previous paragraph. In the figure, the symbol (a) corresponds to the surface shown in Photo. 4 and spreading of BAg-5 filler metal was made

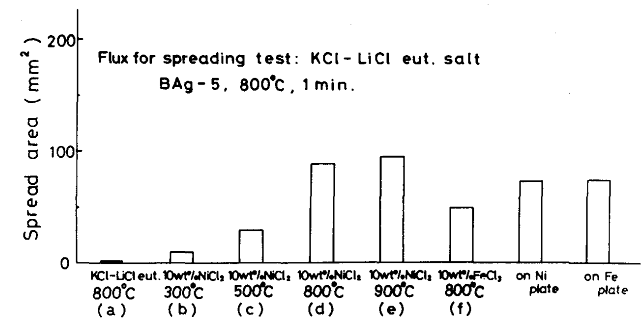

Fig. 1 Comparison of spreading test results.
(a) on suface of Photo. 4, (b) on same surface as Photo. 1 but heating temp. is 300°C, (c) on surface of Photo. 1, (d) on surface of Photo. 2, (e) on surface of Photo. 3, (f) on surface of Photo. 7, and on surfaces of nickel and armco iron plates.

for 1 min. at 800°C. The spread area is zero. The symbol (b) is complemental data for the symboles (c), (d) and (e), respectively, corresponded to the surfaces shown in Photos. 1, 2 and 3. The spread area of these symboles shows evident increasing with temperature, excepting both (d) and (e) saturates. This increasing is considered to be depended the $FeNi_3$ compound fromed on the plate surface as mentioned in previous paragraph, whereas the spread area on the surface of symbol (f) is smaller than that of symbol (d). The surface (f) corresponds to the surface shown in Photo. 7 and there is the $FeNi_3$ compound wholly. Accordingly, the difference of spread area (d) and spread area (f) was attributed to the nickel particle layer which was observed in Photo. 2. Then, the spread area (d) on nickel particle layer was compared with the spread area on smooth surface of nickel plate shown in Fig. 1. The former is larger than the latter. This discrepancy can be attributed mainly to the surface roughness of base plate as following consideration.

The decrease, $\Delta\sigma$, in surface energy based on wetting is given by following equation (1).

$$\Delta\sigma = \sigma_1 K (\cos\theta + 1) \quad \text{.........} (1)^{**}$$

σ_1 ; surface energy of molten filler metal
θ ; contact angle (<90°)
K ; roughness factor

K value is given by the ratio of the total surface area of nickel particles to the surface area of smooth nickel plate. The total semi-spherical surface area of nickel particles which exists on the most outside of nickel particle layer shown in Photo. 2 is about $(1.41 \times 10^{-5}) \times (1.78 \times 10^{8}) = 2510\text{mm}^2$, if a nickel particle is a sphere of 3μm diameter and the arrangement of nickel particles is simple cubic crystal structure, as mentioned in previous paragrph. On the other hand, the surface area of smooth nickel plate is 1600mm^2, because of same size as stainless steel base plate. So, K value becomes about 1.57.

The spread area on the smooth nickel plate as shown in Fig. 1 is 73mm^2. On considering equation (1), the spread area on the surface of nickel particles layer is given by k times the spread area on the surface of smooth nickel plate and it becomes 115cm^2. However, the spread area gained experimentaly on nickel particle layer as shown in (d) of Fig. 1 is 90mm^2. The difference, 25mm^2, between experimental and calculated values may be depended on assuming that the arrangement of nickel particles is simple cubic crystal structure. And also the molten filler metal penetrates into vertical direction of gap among nickel

* The FeNi3 compound fromed the surface does not dissolve into the molten flux, because the nickel particles was not recognized on the surface shown in Photo. 7. Accordingly, this opinion was introduced.

* Though Yu.V. Goryunov[5] gave $\Delta\sigma = \sigma_1 (K \cos\theta - 1)$ for spreading wetting, we gave equation (1) for adhesional wetting in our experiment.

particles.

In Fig. 1, moreover, the spread area on nickel plate is the same value as that on an armco iron plate, and is larger than the spread area on the suface (f) which formed from the $FeNi_3$ compound wholly. From this experimental fact, it was confirmed that generally intermetallic atom force in an intermetallic compound effects wetting force between a filler metal and a base metal, therefore, the wetting force decreases.

Figure 2 shows the spreading test result was made to

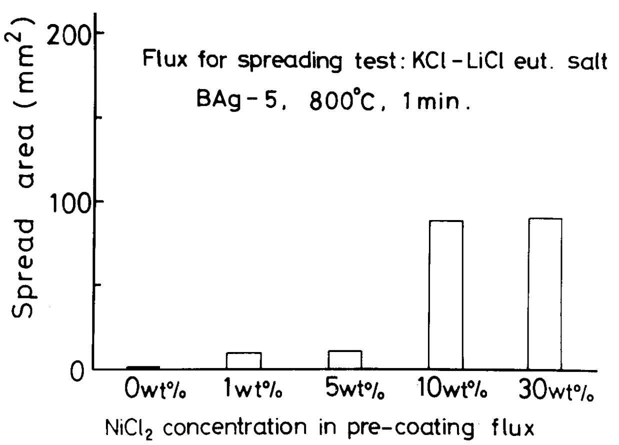

Fig. 2 Effect of concentration of NiCl2 contained in pre-coating fluxes on spreading of BAg-5.

know the concentration effect of $NiCl_2$ added in the mixed flux. The spread area is about equal in spite of the increase of $NiCl_2$ concentration from 10 to 30 percent. This experimental fact showed that the spread was not governed by the thickness of nickel precipitated layer, but by the most outside surface area of nickel particle layers.

In order to confirm above results, the plate surface was precoated with the mixed flux containing 5wt%$NiCl_2$ and heated for 1 min. at 800°C and analyzed by SEM. The result is shown in **Photo**. 8. From this photograph, the surface area occupied with nickel particles is about 60 percent of total surface area pre-coated with the mixed flux. And the remainder is almost the surface of base metal corroded by the mixed flux. So, the addition of 10wt%$NiCl_2$ to 90wt%KCl-LiCl eutectic salt was necessiated to coat the whole surface with nickel particles and gave such saturated spread area as shown in Fig. 2.

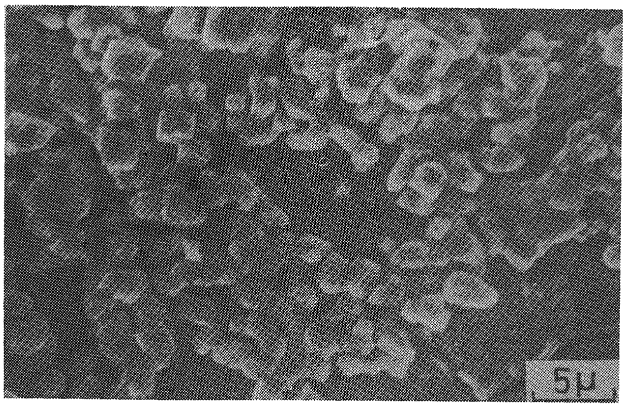

Photo. 8 SEM micrograph of pre-coated surface with flux on 18Cr-8Ni stainless steel plate. Conditions: flux, 5wt% NiCl2 and 95wt% eutectic salt of KCl-LiCl system; heating temp. and time, 800°C, 1 min.

4. Conclusions

In this study, after a stainless steel plate precoated 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 done with KCl-LiCl eutectic salt flux.

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

(1) The addition of $NiCl_2$ to KCl-LiCl eutectic salt promotes the dissolution of chromium and iron from the palte surface of stainless steel and the resultant corroded surface becomes spongy intermetallic compound, $FeNi_3$. Furthermore, the layers of nickel particles on the compound were precipitated by reducing reaction of nickel ions.

(2) The addition of $FeCl_3$ to the eutectic salt also promotes the corrosion of stainless steel and $FeNi_3$ compound only was formed.

(3) The spread area of BAg-5 on the nickel particles layer was considerably larger than that on the compound, $FeNi_3$. This result showed that the wettability of intermetallic compound, $FeNi_3$, is not superior to the each wettability of both constituent elements, Fe and Ni.

(4) The spread area of BAg-5 on the nickel particles layer was larger than that on a nickel plate, because the former was larger than the latter in a real surface area to be wet. Furthermore, since the spread area depended on the total surface area of particles distributed on the most outside layer, the amount of $NiCl_2$ to form mono-particle layer was considered to be about 10wt%.

(5) "De-Chromiumnization" phenomenon on the surface of stainless steel may be one of the important function of fluxes used.

References

1) I. Okamoto, A. Omori and M. Miyake; Studies on Flux Action of Silver Brazing (Report-V), Proc. of Annual meeting of the Japan Welding Society, No. 17 (1975), p284-285. (in Japanese)

2) I. Okamoto, A. Omori and M. Miyake; Studies on Flux Action of Silver Brazing (Report-1), Transactions of J.W.R.I,

vol. 4 (1975), p119-126.
3) I. Okamoto, A. Omori and M. Miyake; Studies on Flux Action of Soldering (VI). J. Japan Welding Society, vol. 43, No. 7 (1974), p35-41. (in Japanese)
4) I. Okamoto, A. Omori et al; Relation between Spreading Area and Penetration Height in Soldering, Transactions of J.W.R.I, vol. 4, No. 2 (1975), p105-111.
5) Yu. V. Goryunov; Physicochemical Features of the Spreading of a Liquid Metal on a Solid Metallic Surface, Russian. Chemical Reviews, Vol. 33, No. 9 (1964), p467-479.