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Studies on Vacuum Brazing (Report II)[†]

—Removal of oxide film from stainless steel surface and brazing alloy spreading mechanism—

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Abstract

Vacuum brazing of stainless steel was studied on both the mechanism of removal of oxide film from stainless steel (SUS304L, SUS3042B, SUS321) surfaces in vacuum heating and the spread mechanism of brazing alloy (BAG-8b) on stainless steel. The surface change of state with vacuum heating was observed by a high temperature optical microscope. The growth and removal of oxide on the surface with heating was clarified. The spreading phenomena were investigated by SEM, EDX, AES and Mass spectroscopy.

The growth of oxide on the surface (SUS304L and SUS3042B) in vacuum heating from 550°C to 750°C was confirmed and the grown oxide was removed with more heating to 860°C, preferentially at the grain boundary part of the surface by reduction reaction of the carbon contained in steel. The phenomenon was confirmed by a striking increase in CO gas in vacuum atmosphere. The spreading of brazing alloy is due to the penetration of alloy into the grain boundary grooves produced by removing the oxide on the surface in vacuum heating. The spreadability was greatly influenced by heating speed in vacuum. Copper or copper-rich alloy diffuses primarily along the grooves without oxide and then liquid brazing alloy easily impregnates them and spreads on the surface. With SUS 321, the removal of oxide film and the formation of grain boundary grooves occur at a temperature of about 900°C which is higher than that for SUS 304L.

KEY WORDS: (Vacuum Brazing) (Silver Alloy) (Spreading) (Mechanism) (Oxide Film)

1. Introduction

As one of the best joining methods for stainless steel, vacuum brazing has been widely used in many industries. As for the vacuum brazing process, two phenomena — the surface state of the base metal changes and brazing alloy spreads on the surface — are greatly important. Usually, the oxide film which exists or is formed on the stainless steel surface disturbs the wetting or spreading with liquid brazing alloy. It is necessary, therefore to remove the oxide from the surface. However, the mechanism of removal of oxide film and the relation between the removal and spreading of brazing alloy were not completely clarified in vacuum brazing.

There are several theories on the removal of oxide film, including: the heat decomposition of oxide in vacuum heating¹⁾, the evaporation of oxide²⁾ reduction of oxide by the carbon contained in steel³⁾⁴⁾⁵⁾ and others.

As spreading mechanism, it is considered that a halo⁶⁾ which shows a reaction between brazing alloy and the substrate, is seen ahead of spreading droplet. The chemical removing of oxide film on copper by phosphorus rich liquid in brazing alloy was also found.

Furthermore, a tunneling mechanism of brazing alloy penetration along oxide film-base metal interface has been reported.⁷⁾⁸⁾ After puncturing or crazing of oxide film on base metal surface, base metal surface was wetted and spread by penetrating along the interface between oxide film and base metal (tunneling) with liquid brazing alloy.

As mentioned above, the spread mechanism is not same for a different combination of brazing alloy and base metal.

In this research, the mechanism of growth and removal of oxide film during vacuum heating was clarified and

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then the relation between the removal of oxide on stainless steel surface and the spreading behavior of brazing alloy on such surface was examined.

2. Specimens and Experimental Procedure

The chemical compositions of stainless steels used are shown in Table 1 – the specimen size was 20 × 20 mm and 2 mm in thickness. The surface was polished with emery paper and then degreased with acetone. As brazing alloy, BAg-8b (Ag-28 wt% Cu-0.5 wt% Ni) was used, the apparatus and method for vacuum brazing were the same as in the previous report⁹⁾. The surface state of stainless steel in vacuum heating was observed with high temperature microscope. The growth and removal of oxide film during vacuum heating was analyzed by AES. The front edge of spread droplet on stainless steel surface was observed by SEM and element analysis was done with EDX and X-ray diffractometer. Residual gas in vacuum furnace and the growth of gas during brazing was analyzed with Quadrupole mass spectrometer.

Table 1. Chemical composition of stainless steel used

Material	Chemical composition (wt %)							
	C	Si	Mn	P	S	Ni	Cr	Others
SUS 304 L	0.020	0.58	0.95	0.028	0.009	9.55	18.16	
SUS 304 2B	0.060	0.64	1.23	0.036	0.006	8.57	18.45	
SUS 321	0.08	1.00	2.00	0.040	0.030	9 - 13	17 - 19	Ti 5×Cr ₄

3. Results and Discussion

3.1. Growth and removal of oxide film on stainless steel surface in vacuum heating

The effect of heating temperature at a constant heating speed (10°C/min) on the growth and the removal of oxide on stainless steel surface was examined in vacuum (5×10^{-5} Torr). The results observed by a high temperature microscope are shown in Fig. 1 for SUS304L and SUS321. From these results, it can be seen that there is no change on the surface of steel in vacuum heating until 550°C. However, the surface of SUS304L was completely brown by about 750°C. At about 780°C, white grain boundary parts started to appear on the surface and the grain boundary grooves were formed. At 860°C, white grain boundary grooves spread over all the surface. Such effects of temperature on the change of the surface state is similar for SUS3042B steel. However, in the case of SUS321, a higher temperature of 900°C was necessary white grain boundary grooves to be formed.

In order to clarify more the surface change, AES analysis of such surface was done. The results are shown in Fig. 2 and Fig. 3 respectively for SUS304L and SUS3042B. From figure 2 (a), (b), a thin oxide film was on the polished surface. However, a thick oxide film formed on the surface heated to 750°C in vacuum as shown in Fig. 1 and was composed mainly of Cr₂O₃ as shown in Fig. 2 (c) (d). However, the thickness of oxide film of Cr₂O₃ decreased on the surface heated to 860°C as shown in Fig. 2 (e) (f). Figure 3, shows similarly results for SUS3043B. By ESCA analysis of the oxidized surface of SUS321, Ti oxide (TiO₂) was formed on the surface as

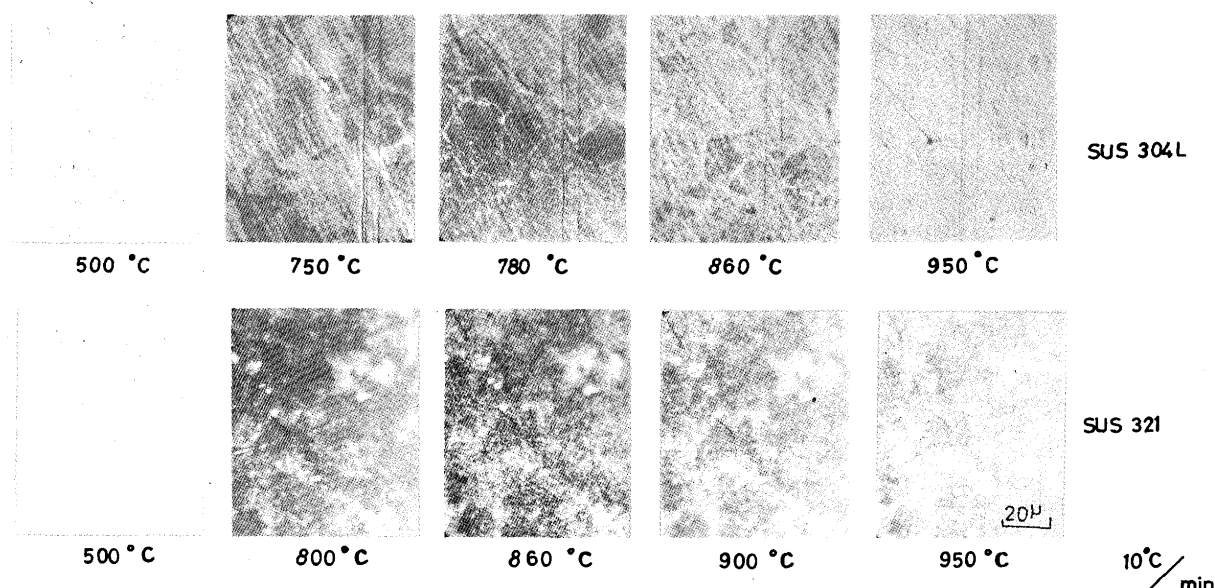
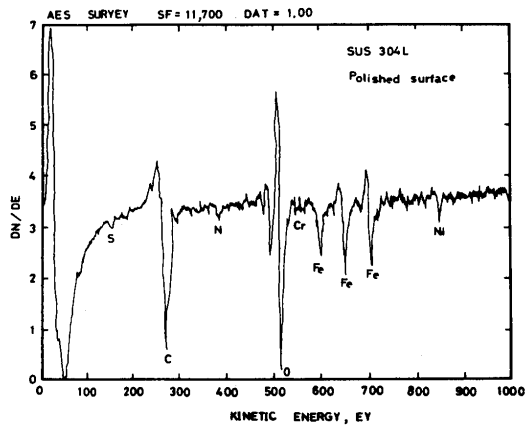
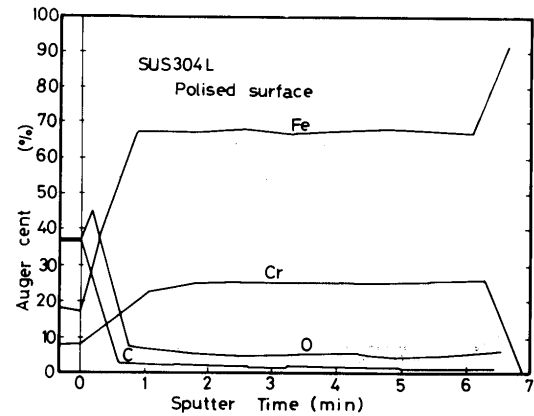


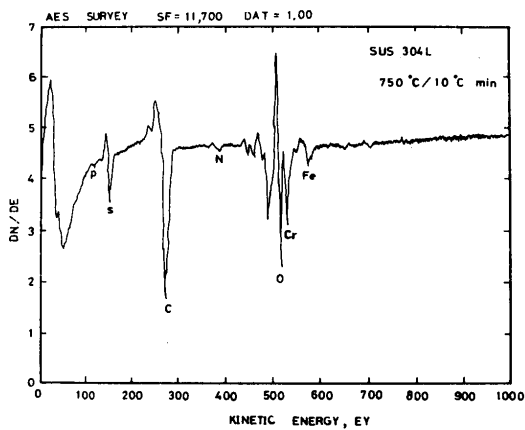
Fig. 1 Effect of heating temperature on change of surface state in vacuum heating under 2×10^{-5} Torr.



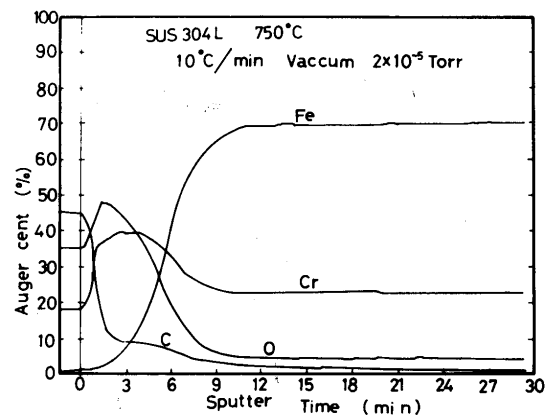
(a)



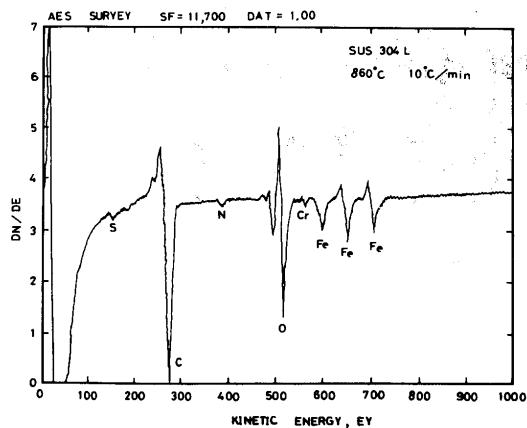
(b)



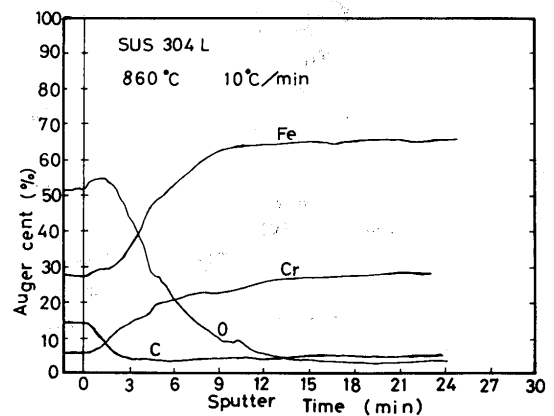
(c)



(d)



(e)



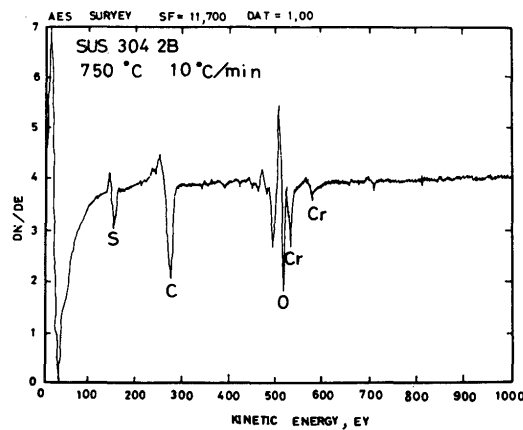
(f)

Fig. 2 AES analysis for polished surface of SUS304L after heat treatment

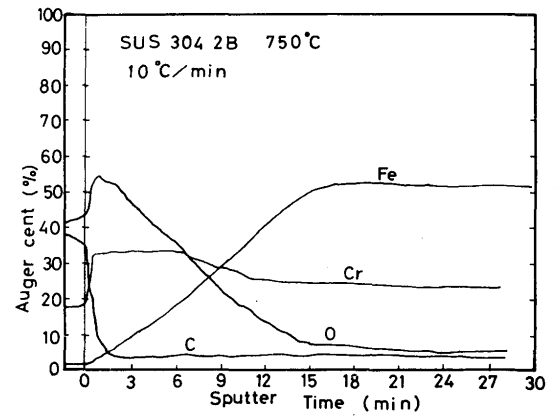
shown in Fig. 4. The oxide cannot be removed by heating at 860°C for 30 min. However, Cr_2O_3 and Fe_2O_3 were removed by heating at 860°C in vacuum.

3.2. Removal mechanism of oxide on stainless steel surface formed by vacuum heating.

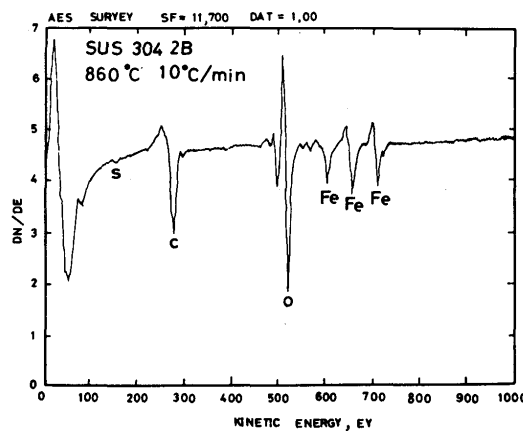
In this experiment, the chromium oxide was formed



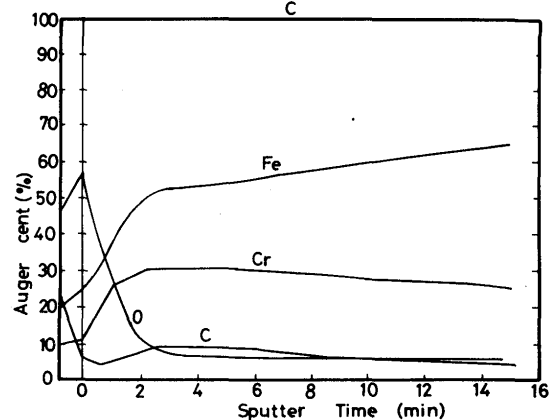
(a)



(b)



(c)



(d)

Fig. 3 AES analysis for polished surface of SUS3042B after heat treatment

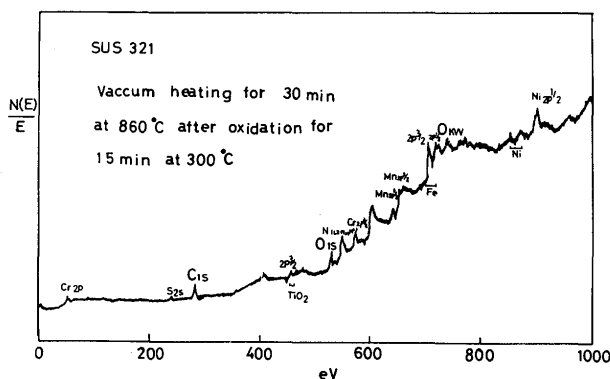
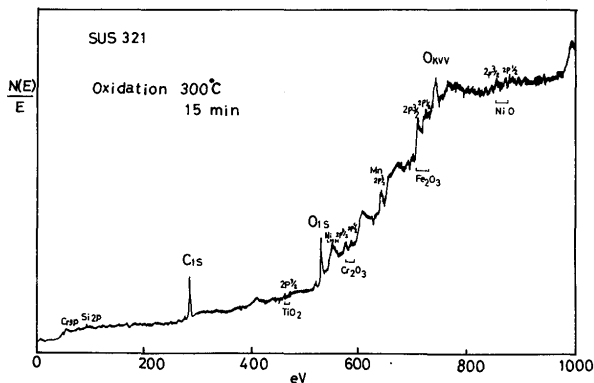


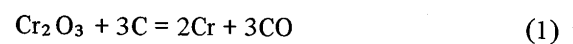
Fig. 4 ESCA analysis for oxidized surface of SUS321 and the surface after heat treatment

mainly on the surface of SUS304L and SUS3042B by heating to 750°C in vacuum.

According to the equilibrium decomposition pressure of metal oxides, it is impossible to decompose Cr oxide until 2000°C by vacuum heating under 2×10^{-5} Torr. However, it was removed from the surface in these experimental conditions (860°C, 2×10^{-5} Torr) as shown in Fig. 2 and Fig. 3. The causes for the removal of the oxide in this experiment may be considered as follows:

Recently, the removal of oxide by the reduction of carbon contained in steel was reported in vacuum brazing for carbon steel⁹⁾ and in vacuum heat treatment for stainless steel³⁾.

In this vacuum heating, the removal of Cr oxide from stainless steel surface was accompanied by decarborizing as shown in Fig. 5. In this experiment, the removal of oxide may have been due to the reduction of oxide by carbon during vacuum brazing. The reduction of Cr_2O_3 by carbon is expressed as follows³⁾.



From the relation between the equilibrium pressure of CO and temperature for eq. (1), Cr oxide may be reduced

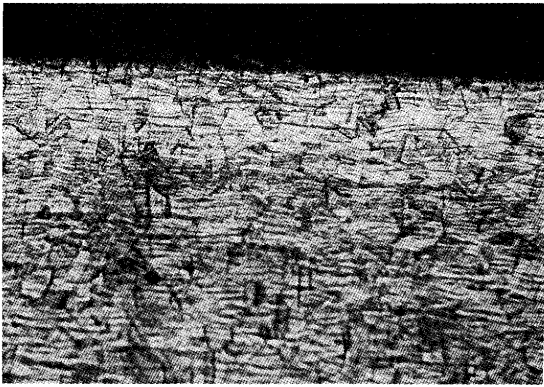


Fig. 5 Decarbonized layer of SUS304L steel after vacuum treatment for 15 min at 900°C for oxidized specimen in air for 15 min at 500°C

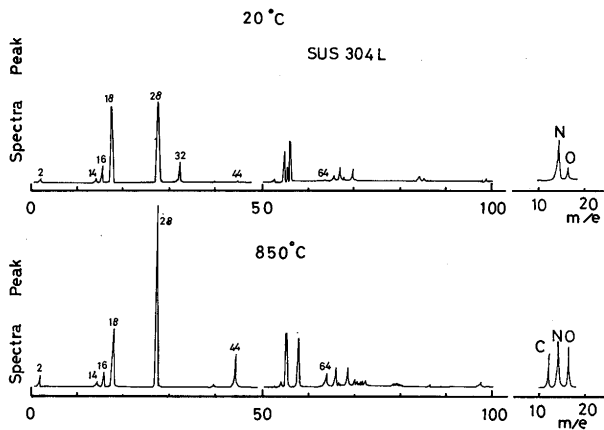


Fig. 6 Analysis results of residual gas in vacuum furnace contained SUS304L stainless steel under 2×10^{-5} Torr.

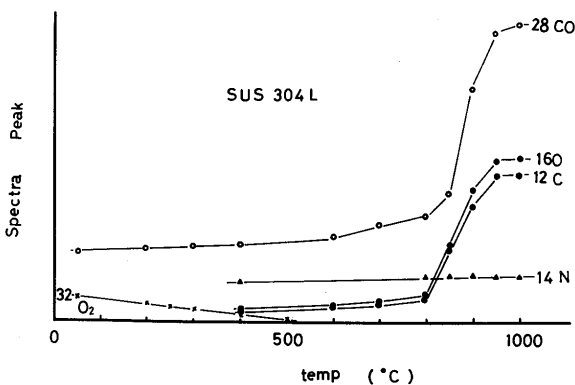


Fig. 7 Temperature dependence of generation of CO gas in vacuum furnace with SUS304L

easily by carbon in stainless steel at 860°C under the vacuum of 2×10^{-5} Torr.

CO and other gases in vacuum atmosphere in heating were analyzed by mass spectrometer at room temperature

and at 850°C, when SUS304L specimen exists in the atmosphere. The results are shown in Fig. 6. From these results, CO gas and CO₂ gas increase when SUS304L specimen was heated to 850°C. However, CO gas does not exist in vacuum atmosphere at R.T. In Fig. 7, the generation of CO gas is shown with an increase of heating temperature in vacuum. From this result, the amount of CO gas increases suddenly at about 860°C. This phenomenon coincides with the formation of grain boundary grooves on all of the SUS304L surface at 860°C.

These results show that Cr₂O₃ produced in vacuum heating to 750°C, is reduced by carbon in steel when heated to 860°C. The reduction occurs near the grain boundary part on the surface, at which the diffusion of carbon in steel is higher than grain part. Grain boundary grooves are seen on the surface of steel and increase with the increase of heating temperature. Table 2 shows the change of carbon on stainless steel (SUS304L) surface after vacuum heating treatment for polished and oxidized specimens.

Table 2. Decrement of carbon content of stainless steel (SUS304L) after vacuum heat treatment for 15 min at 860°C

Vacuum treatment times	Decrement of carbon content		
	No treatment	Oxidation surface	Polished surface
4	1.00	0.87	0.93
8	1.00	0.82	0.86

From this result, carbon content of SUS304L surface decreases more for oxidized surface after heat treatment than for polished or non heat treated surface.

3.3. Spread mechanism of brazing alloy on stainless steel in vacuum heating.

As described above, stainless steel surface (SUS 304L) was oxidized by heating to 750°C in a vacuum of 5×10^{-5} Torr. And then the oxide film formed on the surface was easily removed by more heating to 860°C. In the process of removal of Cr oxide, grain boundary grooves appeared on the stainless steel surface.

During vacuum silver brazing, when such surface change of stainless steel occurs, spreading of brazing alloy may be influenced greatly on such surface of steel. Fig. 8 shows the results of spread test for BAg-8b brazing alloy

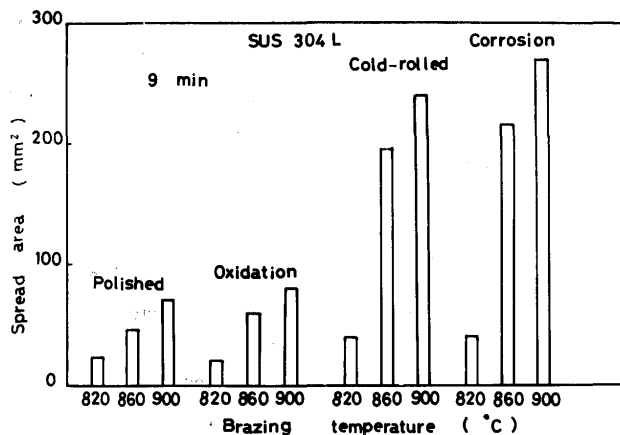


Fig. 8 Spreading area of BA9-8b brazing alloy on differently treated surfaces of SUS304L stainless steel

on differently treated surfaces of SUS304L. From this figure, at 820°C spread is not seen, but spread area increases with heating temperature for both polished and oxidized (300°C 15 min in air) surfaces. However, with the increase of temperature spread increases greater for both as received and corroded (with HNO₃ + HCl solution) surface than for polished and oxidized surface.

In Fig. 9, SEM and EDX analysis results are shown for front part of droplet spreaded at 860°C on SUS304 polished surface. From this figure, the spread is due to penetration of liquid brazing alloy into grain boundary grooves and three regions were seen for spread. More-

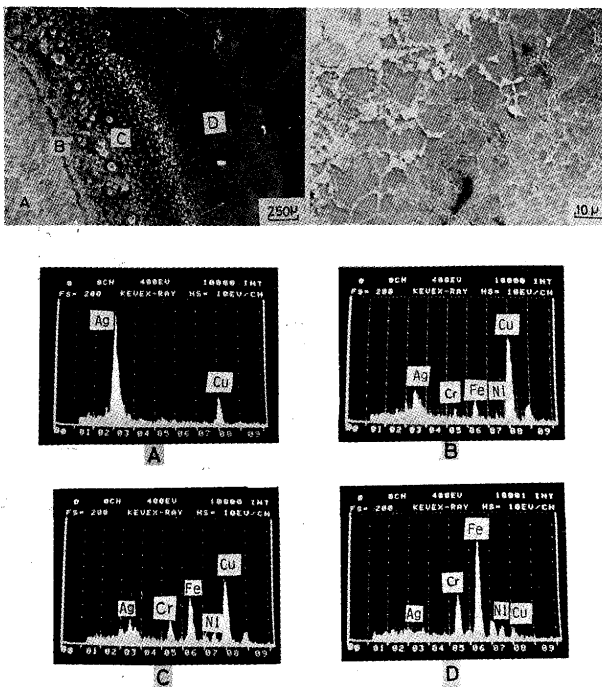


Fig. 9 SEM micrographs of the front-edge of spreading brazing alloy for polished surface of SUS304L stainless steel

over, by the analysis of EDX, the decrement of Ag/Cu ratio in brazing alloy was confirmed from the middle (A part) to the edge (D part) of the spread brazing alloy, that is to say, copper is richer at the front-end of the spread droplet. Copper diffuses mainly into the grain boundary grooves, where oxide film was removed by carbon. This phenomenon cannot be found for spreading at 820°C but can be found clearly for spreading at 900°C. These facts coincide with the fact that the amount of the grain boundary grooves and spread area increases with heating temperature. Fig. 10 shows similar results of spread at 860°C for oxidized surface. From this figure, the penetration of filler metal into grain boundary grooves is acknowledged for oxidized surface by means of removal of oxide film during vacuum brazing. Three regions were also seen. The similar results for as-received and corroded surfaces are shown respectively in Fig. 11 and Fig. 12. Here the spread area increases suddenly at 860°C. The cause is due to grain boundary grooves produced before vacuum heating. And liquid filler metal penetrates easily into the grooves after easy removal of oxide film on the grooves and melting of filler metal. Only two regions were seen for spread. Fig. 13 shows the dependance of heating time on spread area at 860°C for both polished and oxidized surfaces. Spread area increases with the lapse of heating time. The reason is dependent on the increase of

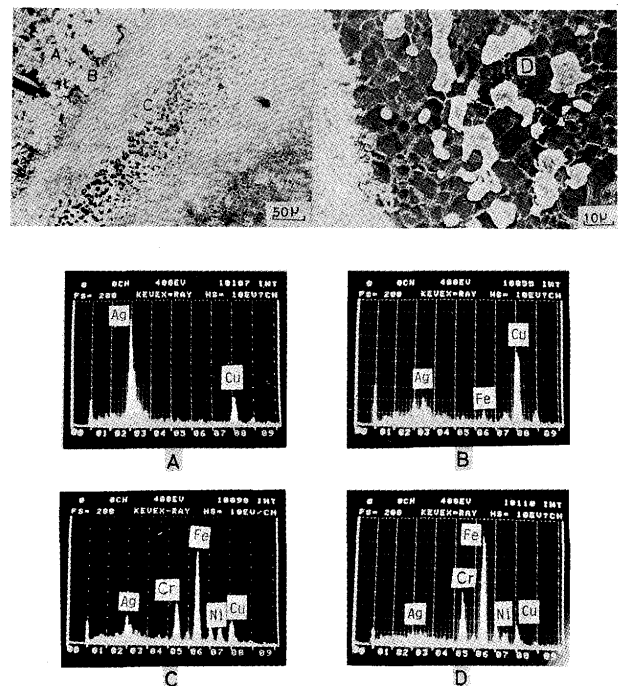


Fig. 10 SEM micrographs of spreading phenomena of BA9-8b brazing alloy on oxidized surface (300°C, 15 min) of stainless steel of SUS304L

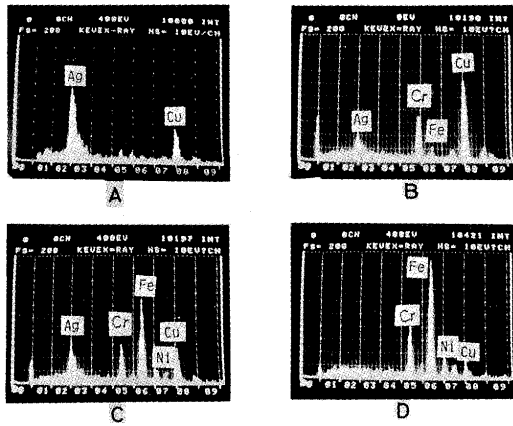
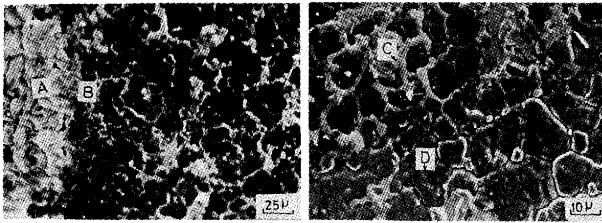


Fig. 11 SEM micrographs of the front-edge of spreading brazing alloy for as-received surface of SUS304L

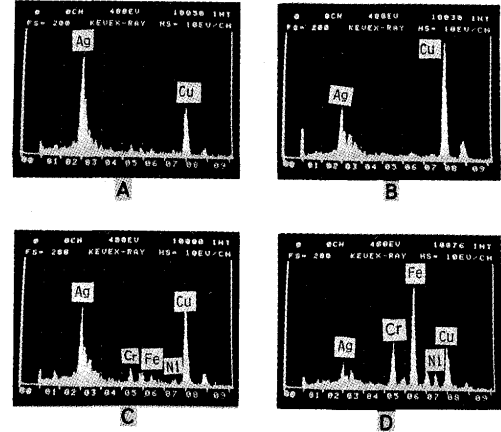
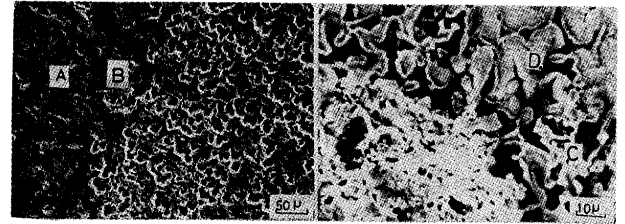


Fig. 12 SEM micrographs of the front edge of spreading brazing alloy for corroded surface of SUS304L

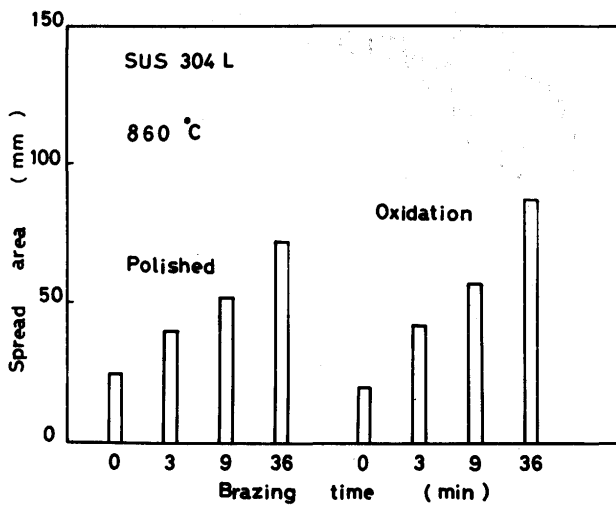


Fig. 13 Effect of brazing time on spreading area of BAG-8b brazing alloy on polished and oxidized surface of SUS304L

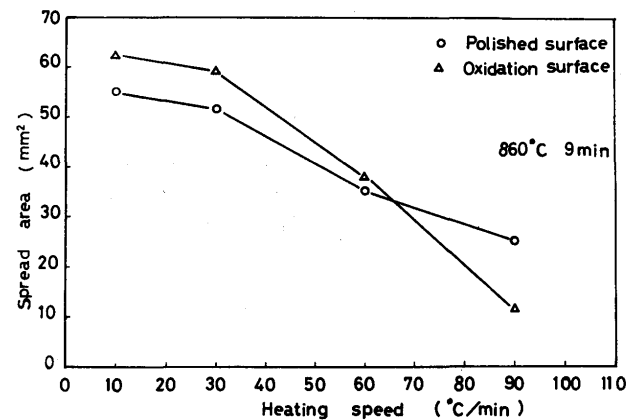


Fig. 14 Heating speed dependence of spread area for polished and oxidized surface of SUS304L

grain boundary grooves on the surface of SUS304L with heating time. Fig. 14 shows the effect of heating speed on the spread area for 9 min. at 860°C for polished and oxidized surface of SUS304L. From this figure, it is known that the spread area decreases with the increase of heating speed. When the heating speed is higher, the removal of oxide film produced during heating becomes more difficult than for slow heating speed. And the grain boundary grooves are not easier to form on the surface, when the heating speed is higher. So the spread area

becomes small at higher heating speed due to decrease of amount of the grooves. Fig. 15 shows the effect of heating temperature on spread area for SUS321 (polished). In this figure, spread area at 860° is smaller than for SUS304L and spread is not seen as at 820°C

However, at 900°C the spread area increases greatly and is similar to spread area at 860°C for SUS304L.

These facts may be depended on the fact that the grain boundary grooves spread on all of the surface of SUS321 at 900°C.

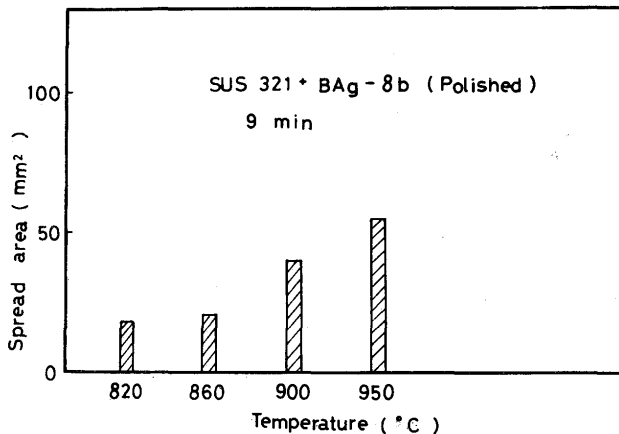


Fig. 15 Effect of heating temperature on spread area on polished SUS321 surface

4. Conclusions

The results of these investigations are summarized as follows:

- (1) Growth of oxide film on stainless steel surface has been observed in vacuum heating under 2×10^{-5} Torr pressure during $500^{\circ}\text{C} \sim 750^{\circ}\text{C}$, after which the removal of such oxide film occurs near the grain boundary mainly by reduction of carbon in stainless steel at higher heat temperature.
- (2) The process of growth and removal of oxide film depends not only on the chemical compositions and surface state of steel, but also on heating temperature, heating time, heating speed and etc.
- (3) The spreading mechanism may be described as follows; Selective diffusion of copper occurs along grain boundary grooves formed by removal of oxide and then melted brazing alloy liquid penetrates into grain boundary grooves. The spread area is improved by the formation of grain boundary grooves on the surface of stainless steel.

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