Title	Studies on Vacuum Brazing (Report III) : Effect of manganese added in sliver-copper brazing alloy on brazability(Welding Physics, Process & Instrument)
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Studies on Vacuum Brazing (Report III)†

–Effect of manganese added in sliver-copper brazing alloy on brazability–

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Abstract

Vacuum brazing of stainless steel was studied on the effect of Mn addition in silver-copper brazing alloy on brazability. The improvement of brazability by the addition of Mn to brazing alloy was discovered on stainless steel surface (SUS304L, SUS321). The spread area increased with the increase of Mn amount in brazing alloy. Particularly, the improvement of spreadability was observed remarkably for SUS321 stainless steel, and pre-oxidized SUS304L stainless steel. The effect of Mn addition in brazing alloy on spreadability was considered as follows; When Mn alloy was used, the grain boundary grooves were easily formed on the stainless steel surface during brazing and then the liquid brazing alloy impregnated them and spread easily on the surface. Because, H_2O and O_2 gas in vacuum atmosphere reduced due to vaporizing of Mn. So, the re-oxidation of stainless steel surface on which the oxide film was removed by vacuum heating was inhibited. Moreover, the deposition of Mn on stainless steel surface assisted the reduction of oxide. Then, the grain boundary grooves formed on such stainless steel surface.

KEY WORDS: (Vacuum Brazing) (Manganese Alloy) (Stainless Steel) (Spreading) (Oxide Film)

1. Introduction

As for the vacuum brazing stainless steel (SUS304), the oxide film which exists or forms on the stainless steel surface during brazing, disturbs the wetting or spread with liquid brazing alloy. The removal of oxide film from stainless steel surface and the brazing alloy spreading mechanism was clarified[1] as follows; 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. The spreading is due to the penetration of the alloy into the grain boundary grooves produced by removing the oxide by the reduction reaction of carbon contained in stainless steel. However, with SUS321 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 SUS304L. In usual cases, stainless steel which contains Ti or Nb is difficult to be wetted or spread with liquid silver-copper brazing alloy about 850°C.

There are some reports[2,3] on the study of the improvement of spreadability by Mn addition to Ag-Cu alloy. However, the effect of Mn on the brazability was not completely clearified.

In this research, the behavior of Mn during vacuum brazing was examined and the effect of Mn on the improvement for spreading was clearified.

2. Specimens and Experimental Procedure

The chemical compositions of brazing Mn alloys and stainless steels used are shown respectively in **Table 1** and **Table 2**. The specimen size of stainless steel was 20 mm diameter and 2 mm thickness. The apparatus and method for vacuum brazing were the same as in the previous report[1]. The front edge of spread droplet on stainless steel was observed by SEM and element analysis was done with EDX and X-ray fluorescent spectrograph. The surface state of stainless steel during vacuum heating was analyzed by ESCA. Residual gases in vacuum furnace during brazing were analyzed with Quadropole mass spectrometer.

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Table 1 Chemical composition of brazing alloy used

Brazing alloy	Chemical composition (wt%)			
	Ag	Mn	Cu	Ni
M - 1	67	3-3.5	30	0.7
M - 2	64	4.5 - 5	31	0.7
M - 3	61	5.5 - 6	33	0.9
BAg-8b	77.5	0	28	0.5

Table 2 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 321	0.08	1.00	2.00	0.040	0.030	9 - 13	17- 19	Ti 5×C%

3. Results and Discussion

3.1 Effect of Mn on brazability

The effect of heating temperature on spread area of BAg-8b for SUS321 is shown in **Fig. 1**. From this figure, spread area at 860°C is smaller than for SUS304L[1]. However, the spread area at 900°C increases greatly and is similar to spread area at 860°C for SUS304L. **Fig. 2** shows the spread area at 860°C for on polished surfaces of SUS304L and SUS321, when various Mn alloys in Table 1 were used. For both stainless steels the spread area increases with increase of Mn amount in brazing alloy and especially the increase tendency of spread area is more remarkable for SUS321 than for SUS304L. **Fig. 3** shows the spread area on the oxidized stainless steel surfaces of SUS304L and SUS321 at 860°C, when various Mn alloys in Table 1 were used. From this figure, the spread area increases with increase of Mn amount in the alloy. The increase degree of spread area is greater for SUS321 than for SUS304L. Moreover, spread area for oxidized surface is greater than for polished surface. The effect of pre-oxidation temperature on spread area of M-3 alloy is shown in **Fig. 4** for SUS321. The spread area shows maximum value at 500°C of oxidation temperature of SUS321. It decreases with the raise of oxidation temperature from 500°C to 700°C. From various spread test results, the improvement of spreadability by Mn addition in Cu-Ag alloy was seen. The effect of Mn addition is remarkable for SUS321 stainless steel.

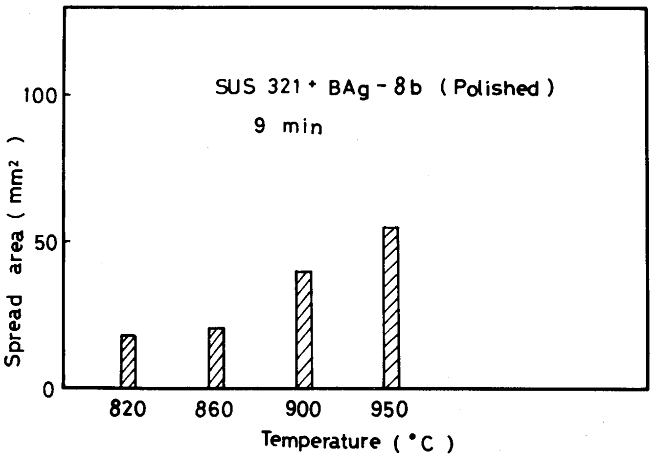

Fig. 1 Effect of brazing temperature on spread area of BAg-8b brazing alloy on polished surface of SUS321

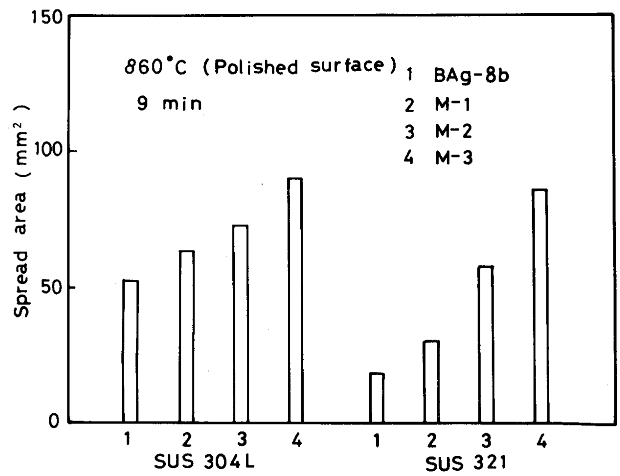

Fig. 2 Effect of Mn addition in brazing alloy on spread area at 860°C on polished surfaces of SUS304L and SUS321

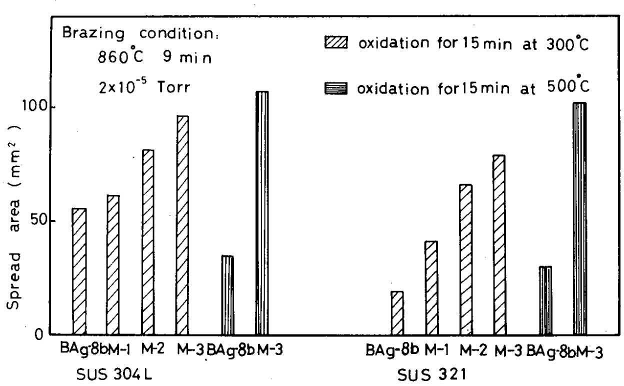

Fig. 3 Effect of Mn addition in brazing alloy on spread area at 860°C on oxidized surfaces of SUS304L and SUS321

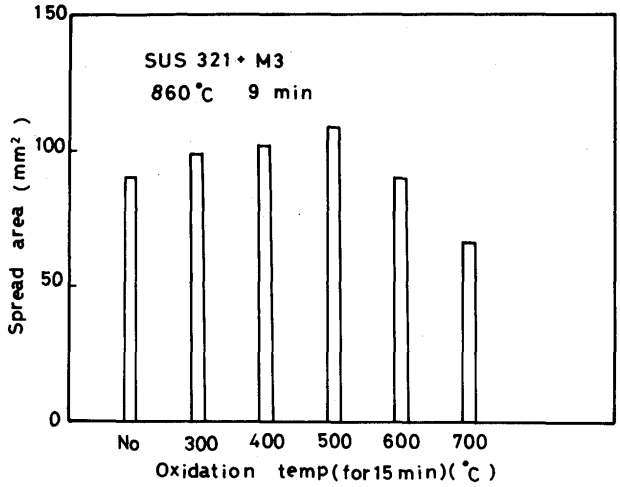

Fig. 4 Effect of pre-oxidation temperature of SUS321 on spread area of M-3 alloy at 860°C

3.2 Behavior of spread front edge of liquid brazing alloy

For the surface of SUS304L stainless steel oxidized for 15 min at 500°C, liquid BAg-8b without Mn is difficult to spread on the surface at 860°C, because oxide film was not removed and grain boundary grooves were not formed on the surface. However, liquid M-3 alloy with Mn spread easily on the oxidized surface of both SUS304L and SUS321. So, the behavior of spread front-edge of liquid droplet alloy was observed by SEM for polished surface of SUS304L and SUS321. The results were shown in **Fig. 5 (a) (b)**. For SUS304L, the penetration of liquid both BAg-8b and M-3 alloy into grain boundary grooves was seen after spread test of 9 min at 860°C. However, for SUS321 the penetration of BAg-8b alloy was not seen for the specimen spread at 860°C. But liquid M-3 alloy penetrated into them at same spread conditions. From figure 2, spread area for M-3 alloy becomes bigger than for BAg-8b, which does not penetrate into grain boundary grooves. **Fig. 6** shows SEM-results of spread front edge for 9 min at 860°C on the surface oxidized at 300°C of SUS304L and SUS321 when BAg-8b and M-3 alloy were used. From this figure, the liquid BAg-8b alloy impregnates into grain boundary grooves for SUS304L, but it does not impregnate into them for SUS321. However, the liquid M-3 alloy can impregnate them even for SUS321.

From above results, the effect of Mn addition in brazing alloy on spreadability is due to the formation of grain boundary grooves and the penetration of the liquid alloy in them. So, spread area increases greatly in the case of brazing alloy with Mn. Also, the improvement of spreadability for surface oxidized at 500°C of SUS304L and SUS321 is dependent on the formation of grain boundary grooves by Mn addition.

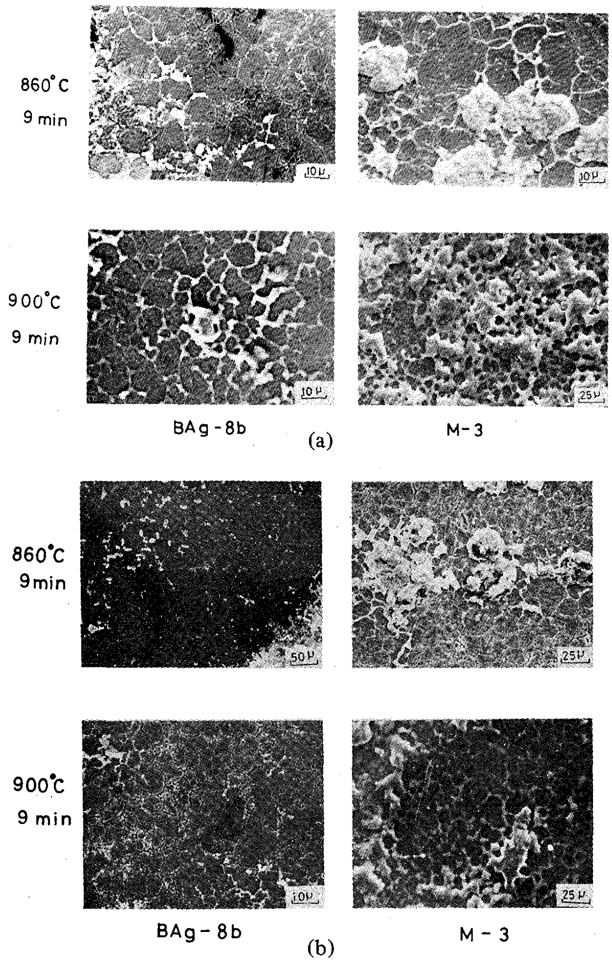

Fig. 5 SEM micrographs of the front-edge of spreading for BAg-8b and M-3 alloy on polished surfaces of SUS304L (a) and SUS321 (b)

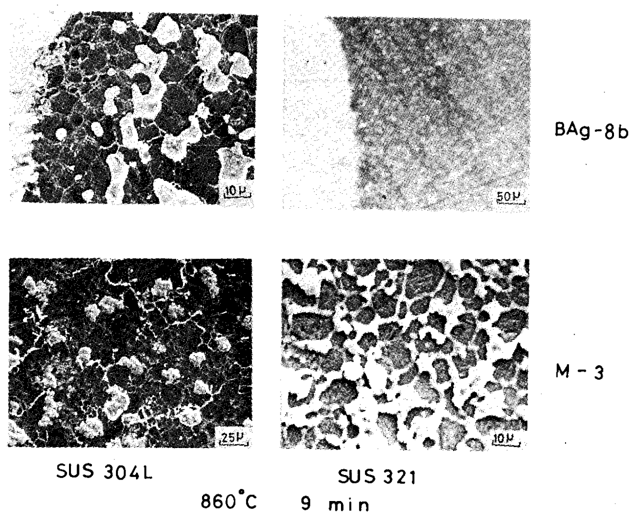

Fig. 6 SEM micrographs of the front-edge of spreading for BAg-8b and M-3 alloy on surfaces oxidized for 15 mm at 300°C of SUS304L and SUS321

3.3 Effect of Mn on spreadability

The improvement of spreadability is due to the formation of the grain boundary grooves on the surface of SUS321 by Mn during spreading. The formation of the grain boundary grooves may be based on removing of oxide film by reduction action of Mn.

The oxide film of SUS321 was composed mainly with TiO_2 as shown in the previous report[1]. The oxide film was not removed completely by this vacuum heating. Even if the oxide film is removed at a grain boundary part, the surface part may be re-oxidized immediately, because Ti oxidizes easily. However, the grain boundary grooves were formed on the surface and re-oxidation did not occur and liquid alloy spread easily on the surface, when Mn was present in the brazing atmosphere. So, gases in vacuum atmosphere at 20°C, 750°C and 850°C were analyzed by mass spectrometer, when Mn brazing alloy existed in the atmosphere.

The results are shown in **Fig. 7**. At 20°C, there were much H_2O and O_2 in the atmosphere. However, the decrease of H_2O and O_2 gases was seen in the atmosphere at 750°C and 850°C, and Mn, MnO, MnO_2 existed. Namely, the re-oxidation of SUS321 surface was protected by the decrease of H_2O and O_2 gases due to the reaction between these gases and Mn which vaporized from M-3 alloy during brazing. Also, the deposition of Mn

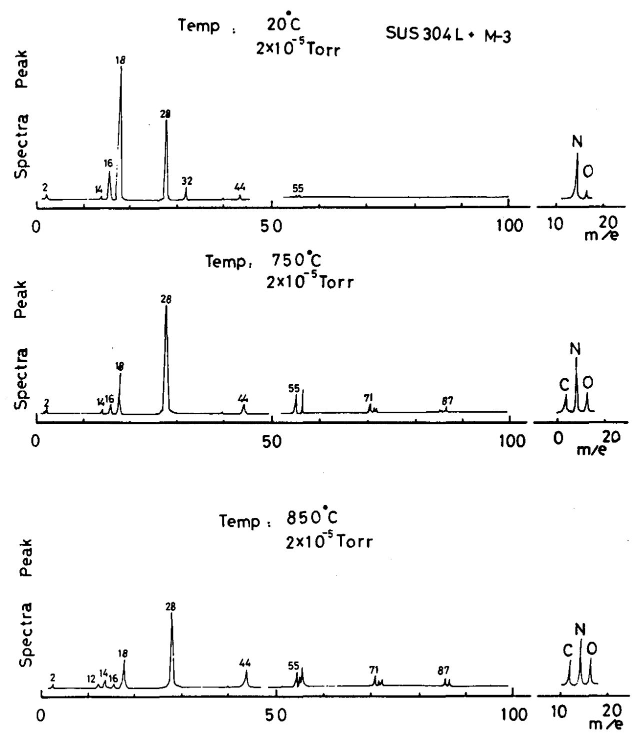

Fig. 7 Analysis results of residual gases in vacuum atmosphere with both SUS304L and M-3 alloy at various temperatures

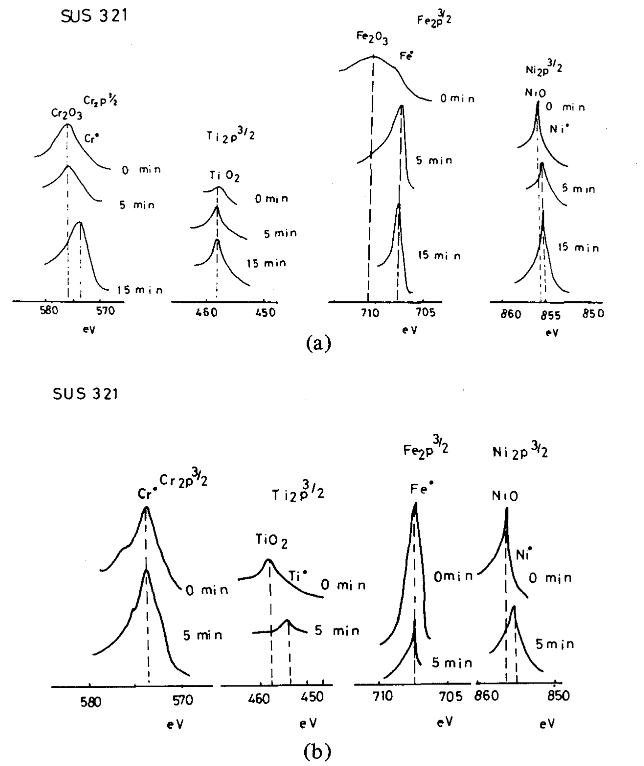

Fig. 8 ESCA analysis for the SUS321 surface oxidized for 15 min at 300°C (a) and the oxidized surface (b) after heat treatment for 30 min at 860°C with M-3 alloy in vacuum

was confirmed on the stainless steel surface by X-ray fluorescent analysis. By the deposition of Mn, the oxide such as Cr_2O_3, TiO_2 may be reduced. So, the SUS321 surface oxidized for 15 min at 300°C was analyzed by ESCA analysis and also the oxidized surface was analyzed after heat treatment for 30 min at 860°C with M-3 alloy in vacuum.

The results are shown in **Fig. 8 (a) (b)**. In figure, 0, 5 and 15 min are Ar^+ sputter times done before ESCA analysis. From Fig. 8 (a), the oxide films are composed mainly with Fe_2O_3, Cr_2O_3, NiO and TiO_2. However, Cr_2O_3 disappears and the thickness of TiO_2 film on the oxidized surface decreases by such heat treatment with M-3 alloy.

From these analyses, it was confirmed that oxides such as TiO_2, Cr_2O_3 were removed easily on SUS321 surface by vaporizing and deposition of Mn when M-3 alloy contained Mn was used for brazing.

Next, the contact surfaces of SUS304L contacted respectively with M-3 and BAg-8b alloy were observed after heat treatment for 15 min at 700°C in vacuum without melting of both alloys.

The results are shown in **Fig. 9**. As shown in this figure, the formation of grain boundary grooves are seen on both polished and oxidized surface of SUS304L only in the

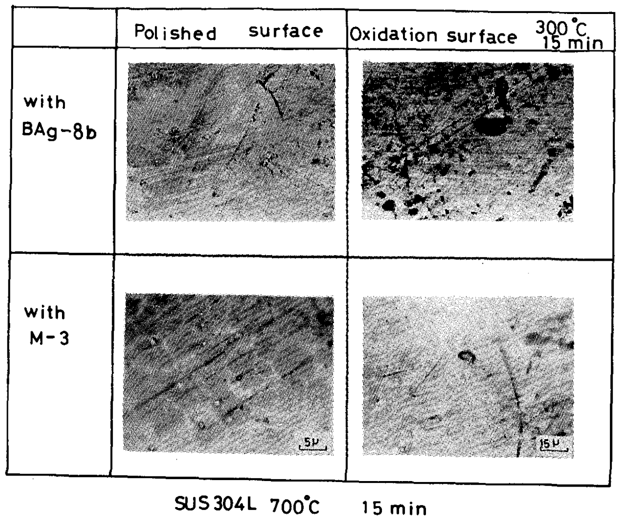

Fig. 9 Photomicrograph of the contact surface of SUS304L after heat treatment for 15 min at 700°C in contact with BAg-8b and M-3 alloy

case of M-3 alloy even at lower temperature of 700°C. It was recognized that Mn contributes greatly to the formation of grain boundary grooves on the surface of stainless steel.

From above results, the improvement of spreadability by Mn is due to the formation of grain boundary grooves by the reduction of oxide and the inhibition of re-oxidation of stainless steel surface. The oxides such as TiO_2, Cr_2O_3 are reduced by the deposition of Mn. The re-oxidation is inhibited due to removal of H_2O and O_2 gases in atmosphere by vaporization of Mn.

4. Conclusions

The results of these investigation are summarized as follows:

(1) The improvement of spreadability has been observed on oxidized surface of SUS304L and SUS321, when Cu-Ag brazing alloy containing Mn (3-6wt%) is used

(2) The improvement is due to the penetration of liquid brazing alloy into the grain boundary grooves which are formed on the surface of stainless steels.

(3) The effect of Mn on spreadability is dependent on the removal of oxides such as Cr_2O_3, TiO_2 for SUS321 by the reduction reaction of Mn, and the decrease of H_2O and O_2 gases in brazing atmosphere by vaporization of Mn.

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