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# Corrosion Behaviour of Silver Brazed Stainless Steel in Chloride Solutions<sup>†</sup>

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## Abstract

The corrosion behaviour of silver brazed SUS 304 stainless steel has been studied in 0.4 mol/l NaCl solutions with additions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  up to 0.05 mol/l. The effects of filler alloy composition and the copper in solutions on the corrosion behaviour were discussed. Simultaneous corrosion of filler alloy and stainless steel at brazed interface took place. To evaluate each corrosion rate, a new stainless steel specimen shape, in which the molten filler alloys were flown along a groove with the radius of 2.5 mm, was used. Major elements of filler alloys and stainless steel except silver were dissolved into the solution. The corrosion of brazed filler alloy was the preferential dissolution of  $\alpha$ -Cu (mainly Cu-Zn) phase. Filler alloys containing cadmium and indium had lesser corrosion resistance than Ag-Cu-Zn ternary alloys and exhibited rapid interfacial corrosion.

The corrosion rates of filler alloys and interface were found to depend greatly on the copper content in chloride solution. The copper increased the corrosion rate mainly by the enhancement of cathodic reaction. Over the range of this study, BAg-4 filler alloy was suitable for the corrosion resistant SUS 304 braze joint.

**KEY WORDS:** (Corrosion tests) (Brazed joints) (Brazing fillers) (Austenitic stainless steels) (Halides)

## 1. Introduction

Silver brazed stainless steel joints has been used as corrosion resistant parts of various joints. But the using circumstances are not always tolerable for the joints, then the failure in acids, chloride solutions, alkaline water and various gas atmosphere cause the troublesome problems in commercial use.

Sistare et al.<sup>1)</sup> used 40 filler alloys of various compositions for the corrosion tests of brazed specimens. Their results emphasised the effect of oxygen concentration cell, however, the galvanic corrosion might influence because the dissimilar alloys of different potentials are coexisted in close contact. Kawakatsu<sup>2)</sup> evaluated the progress of corrosion by the decrease of lap joint strength. But in the lap joints, the voids and liquations may cause the difficulty for the precise evaluation of corrosion resistance. The precise mechanism of the corrosion of the silver brazed stainless steel has not been clarified. Moreover, the estimation method for the degree of corrosion has not been established yet. In this investigation, to elucidate the corrosion mechanism, microscopic and electrochemical studies were carried out using commercial filler alloys of various compositions.

## 2. Suitable Shape for Corrosion Test Specimen

The interfacial corrosion of silver brazed pipe joints seems to be the most detrimental attack in commercial use. Therefore, the pipe joints must be adopted for the corrosion test. However, the overlap of the pipe joints makes liquation of molten filler alloy and moreover makes voids at the brazed part, which brings the difficulty for the evaluation of the degree of interfacial corrosion. Therefore, a new type specimen, which is free from voids at brazed parts and makes no liquation, was used in this study.

## 3. Experimental Procedures

### 3.1 Materials

Figure 1 shows the shape and size of the machined SUS 304 stainless steel specimen. After degreasing, the groove was fluxed with commercial flux and then both ends were blocked by aluminum cement. The filler alloy ( $2\phi \times 55\text{ l mm}$ ) was preplaced along the groove and then heated in air by an electric furnace up to each temperature shown in Table 1. The filler alloy was melted in the groove and the obtained specimen by this procedure was free from

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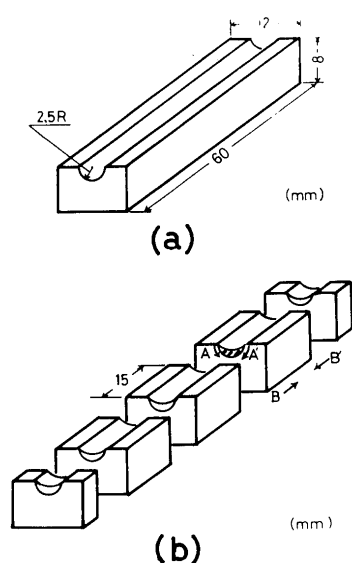


Fig. 1 Shape and size of specimen.

voids at brazed parts and liquations. In this literature, this procedure is designated "brazing". Table 1 shows the nominal chemical compositions of the filler alloys used. The brazing temperatures shown in Table 1 were selected under consideration of the melting temperature range of each filler alloy. The specimens were air cooled after holding for 1 min at the brazing temperature, then cut into five parts as shown in Fig. 1(b), and the central three specimens were used for corrosion tests.

### 3.2 Corrosion Test

After brushing and ultrasonic rinsing in warm water to remove the residual flux, the whole specimen surface was polished by emery paper except the groove. Then the

cleaned specimen was immersed in a pylex bottle containing 100 ml corrosive solution. The test temperature was maintained at 25°C in a thermostat. The corrosive solutions are 0.4 mol/l NaCl aqueous solution containing 0 ~ 0.05 mol/l  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . The compositions are shown in Table 2. After immersion in each solution, the specimens were cut at the longitudinal center to observe the interfacial corrosion proceeded to AA' direction (Fig. 1(b)). Corrosion is also advanced along BB' direction, however, this corrosion length is negligible because the longitudinal length (15 mm) is long enough compared to the corrosion length (~4 mm).

Table 2 Chemical compositions of corrosive solutions.

Solutions	NaCl (mol/l)	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (mol/l)
A	1.0	0.0
A-1	0.4	0.0
B-1	0.4	0.0005
B-2	0.4	0.005
B-3	0.4	0.05

### 3.3 Measurement of Polarization Curves

Electrochemical characteristics in the corrosive solutions were measured by the potentiostatic polarization method in open air condition using platinum counter electrode. The polarization curves were obtained by the potential step of 25 mV/min. Prior to the polarization tests, the specimen surface was polished by 800 grade emery paper and was coated by vinyl resin exclusive of 1  $\text{cm}^2$ . The saturated calomel electrode (S. C. E.) was used as a reference electrode.

Table 1 Nominal chemical composition (wt %) and brazing temperature of filler alloys.

Filler alloys	Ag	Cu	Zn	Others	Brazing temp. (°C)
B-Ag-1a	49 - 51	14.5 - 16.5	14.5 - 18.5	Cd 17 - 19	710
B-Ag-3	49 - 51	14.5 - 16.5	13.5 - 17.5	Cd 15 - 17, Ni 2.5 - 3.5	770
B-Ag-4	39 - 41	29 - 31	26 - 30	Ni 1.5 - 2.5	830
B-Ag-5	44 - 46	29 - 31	23 - 27		795
B-Ag-7	55 - 57	21 - 23	15 - 19	Sn 5	700
T-1	30	38	27	In 5	805
T-2	40	30	25	In 5	765
T-3	34	35	30	In 1	800
T-4	28	35	32	Sn 1, Mn 3, Si 1	805

## 4. Results and Discussions

### 4.1 Observation of Corrosion

Figure 2 shows the schematic illustration of the corrosion profile of BAg brazed stainless steel after immersion in chloride solutions for several days. Two types of corrosion, the preferential dissolution of  $\alpha$ -Cu (mainly consist of Cu-Zn) phase and the interfacial corrosion of stainless steel at the brazed interface were arised from this test. Photograph 1 shows the cross-section of the specimen brazed with BAg-5 filler alloy after corrosion test in B-2 solution for 6 days. Preferential dissolution of  $\alpha$ -Cu phase from the surface was clearly shown. The degree of corrosion of both types was dependent on the chemical composition of silver filler alloy, the copper content in chloride solutions and the immersion time.

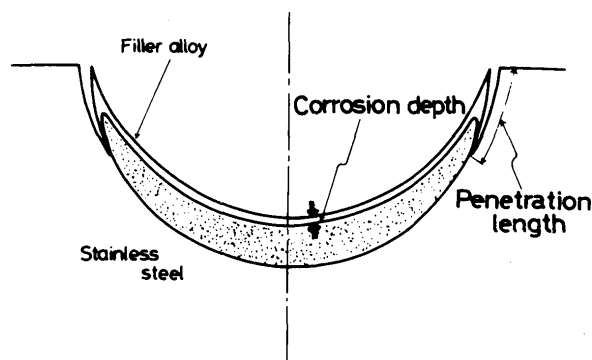


Fig. 2 Schematic illustration of corrosion of silver brazed stainless steel.

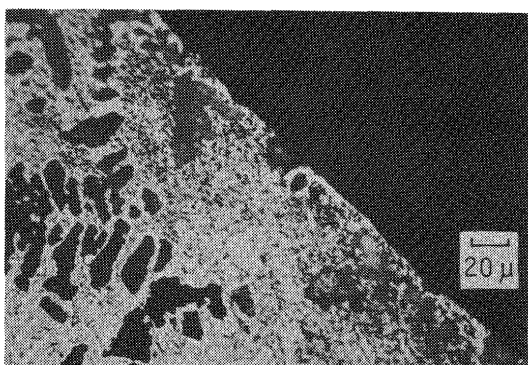


Photo. 1 Micrograph of BAg-5 after corrosion in B-2 solution for 6 days.

The atomic absorption analysis of the corrosive solutions after immersion were carried out to reveal the dissolved element. Table 3 and 4 show the amount of the soluble components and the insoluble deposits. Because the corrosion products and the deposited copper attached

to the specimen surface were not removed and not collected, the strict compositions are not attained. But the tables show the characteristics of the corrosion reactions, and also show that the main elements of both stainless steel and filler alloys except silver were dissolved into the corrosive solution. Preconcentrated cupric ions by the addition of cupric chloride precipitate on the specimen surface during corrosion tests by cathodic reaction. Therefore, the copper concentration in the B-2 solution (initially about 3,000 ppm) was decreased to some extent. But the selective dissolution of  $\alpha$ -Cu phase was identified by microscopic observations and the copper is detected in the solution A which is not preconcentrated by copper, then the copper in  $\alpha$ -Cu phase was really dissolved into the corrosive solution. Only in one case, the trace of silver was detected in the deposit collected from solution A (Table 4). This may be attributable to the falling off of the isolated  $\alpha_1$ -Ag phase by the preferential dissolution of surrounding  $\alpha$ -Cu phase. Because the insoluble deposits collected from solution A was a very small quantity, they were dissolved into 100 ml HCl, therefore the analytical results shown in Table 4 is the composition after dissolving in that solution. From the tables, it is known that major constituent of both stainless steel and filler alloys were dissolved into corrosive solutions.

### 4.2 Corrosion of Filler Alloys

Photograph 2 shows the microstructure of the specimens after immersion tests in B-3 solution for 3 days. The degree of corrosion of filler alloy was relatively slight in BAg type filler alloys but severe in T-1 ~ T-4 filler alloys. The corroded areas of T-1 and T-4 filler alloys are clearly shown by the bright contrast in the upper side of filler alloys (Photo. 2(b) and (c) respectively). Corrosion of T-1 and T-4 filler alloys were also proceeded by the preferential dissolution of  $\alpha$ -Cu phase. Figure 3 shows the results of line analysis of the cross-section of T-1 filler alloy after corrosion tests by electron probe microanalyser (EPMA). Remarkable zinc depleted zone was observed. After the dissolution of  $\alpha$ -Cu phase, copper was deposited on the cathode site (for example,  $\alpha_1$ -Ag phase) by cathodic reaction, then the apparent corrosion profile was resemble to the dezincification of brass<sup>3),4)</sup>. In fact, the used solution causes the dezincification of  $\alpha$ -brass<sup>4)</sup>, however, the study on the mechanism of dezincification is not included in this investigation. Figure 3 also shows that T-1 filler alloy is consisted of Ag-In phase and Cu-Zn phase. Fig. 4 shows the concentration distribution of BAg-5 after immersion in B-3 solution for 3 days. Similarly to T-1 filler alloy, the selective dissolution of  $\alpha$ -Cu phase and the deposition of copper led the zinc

**Table 3** Atomic absorption analysis of corrosive solutions and chemical analysis of corrosion products after corrosion in solution B-3.

Filler alloys	Solution (ppm)							Deposit (ppm, * %)					
	Zn	Cu	Fe	Cr	Ni	Ag	In	Zn	Cu*	Fe*	Cr*	Ni	Ag
BAG-4	187	2350	281	65	65	ND	—	267	38.9	6.1	4.4	44	ND
BAG-5	180	2130	438	128	78	ND	—	147	37.7	8.0	3.5	ND	ND
BAG-7	26	2310	406	117	85	ND	—	44	73.0	9.3	4.7	ND	ND
T-1	833	2000	25	1	10	ND	70	1370	19.0	0.9	0.6	ND	ND
T-2	247	2150	500	128	75	ND	67	270	38.9	6.9	3.5	ND	ND
T-3	526	2150	188	38	40	ND	60	774	40.0	5.8	3.0	19	ND
T-4	473	2250	145	12	30	ND	—	685	42.8	3.8	2.6	ND	ND

ND: Not detected

**Table 4** Atomic absorption analysis of corrosive solutions and chemical analysis of corrosion products after corrosion in solution A.

Filler alloys	Solution (ppm)							Deposit* (ppm)					
	Zn	Cu	Fe	Cr	Ni	Ag	In	Zn	Cu	Fe	Cr	Ni	Ag
BAG-4	4.1	0.04	0.06	ND	1.2	ND	—	1.3	2.8	2.4	0.3	0.6	ND
BAG-5	1.1	ND	0.07	0.03	1.5	ND	—	4.1	8.6	23.2	1.8	1.4	ND
BAG-7	2.5	0.12	0.1	ND	0.2	ND	—	1.2	2.4	2.6	0.2	0.1	tr.
T-1	1.5	0.07	0.1	ND	0.2	ND	107	1.2	2.0	2.9	0.3	0.5	ND
T-2	3.7	0.02	0.1	0.04	0.4	ND	105	1.2	1.9	2.0	0.2	0.1	ND
T-3	4.1	0.04	0.1	ND	1.0	ND	106	7.9	6.5	20.3	1.7	1.4	ND
T-4	0.5	0.15	0.1	0.03	ND	ND	—	2.2	2.6	2.5	0.2	0.4	ND

ND: Not detected      tr. &lt; 0.01

\* analyzed after dissolved in 100ml HCl

depleted area, but the corrosion depth was remarkably smaller than that of T-1 filler alloy. Optical microscopic measurement of the corrosion depth was consistent with the measurement by EPMA. The corrosion depth was increased by the increase in the copper concentration of the corrosive solutions and testing time. For example, the corrosion of T-1 filler alloy after 6 days' immersion in A-1 and B-1 solutions was scarcely observed, but in B-2 and B-3 solutions, the corrosion depths were  $60\mu$  and  $600\mu$  respectively. The relation between the corrosion depth and the immersion time obeyed the parabolic law.

#### 4.3 Interfacial Corrosion

The troublesome problem in the usual usage of the silver brazed stainless steel joint might be the interfacial corrosion. The degree of corrosion is tightly dependent on the reliability of brazement. **Photograph 3** shows the corrosion at BAG-5/SUS 304 interface. In the solution containing 0.005 mol/l or less copper, interfacial corrosion is

proceeded by the restricted width, and the penetration depth was also confined to a certain extent. But in B-3 solution of 0.05 mol/l copper, stainless steel is severely attacked at the brazed interface. The relations between the penetration length (interfacial corrosion length) and the immersion time in various copper content solutions are shown in **Fig. 5** using BAG-5 filler alloy. The penetration length was only the order of one hundred microns in B-1 solution of 0.0005 mol/l copper when immersed for up to 18 days. But in B-3 solution of 0.05 mol/l copper the specimens were subjected rapid corrosion, and the interfacial corrosion was penetrated through the whole interface even by the immersion for about 6 days. Penetration length in the 1.0 mol/l NaCl solution (not containing pre-concentrated cupric ions) was about 0.5 mm for 20.5 days' immersion. Therefore, the addition of cupric ions to NaCl solution greatly enhanced the interfacial corrosion length. **Figure 6** shows the relations between the penetration length and the immersion time in various solu-

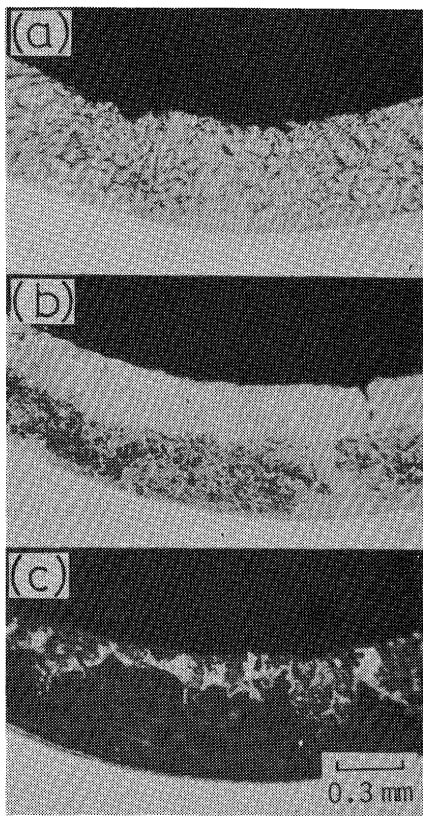


Photo. 2 Micrograph of BAg-5 (a), T-1 (b) and T-4 (c) Filler alloys after corrosion in B-3 solution for 3 days.

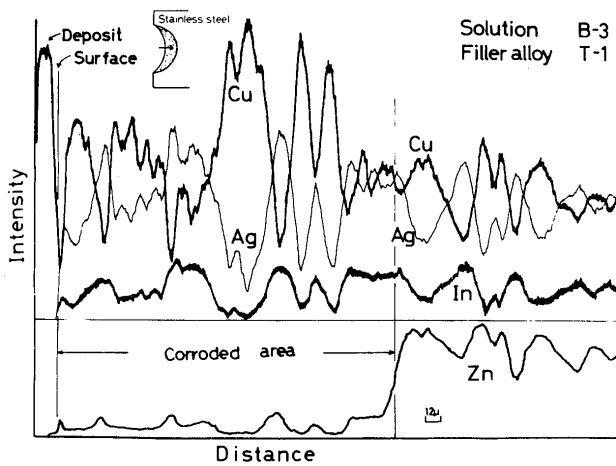


Fig. 3 EPMA of T-1 immersed in B-3 solution for 3 days.

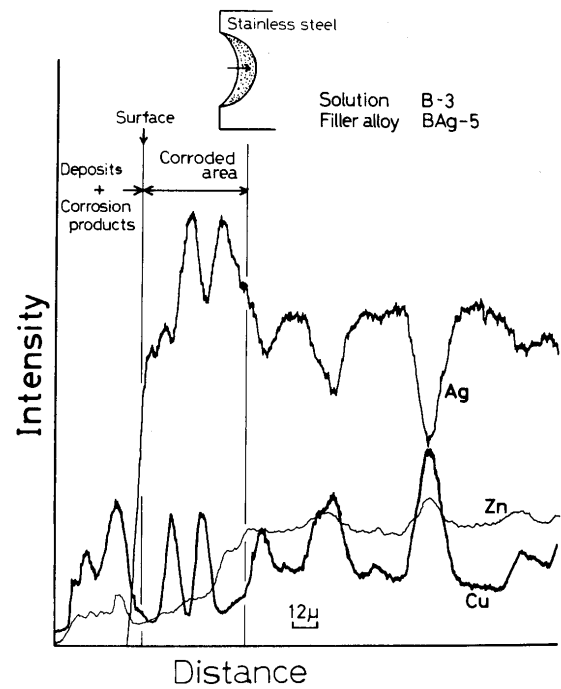


Fig. 4 EPMA of BAg-5 immersed in B-3 solution for 3 days.

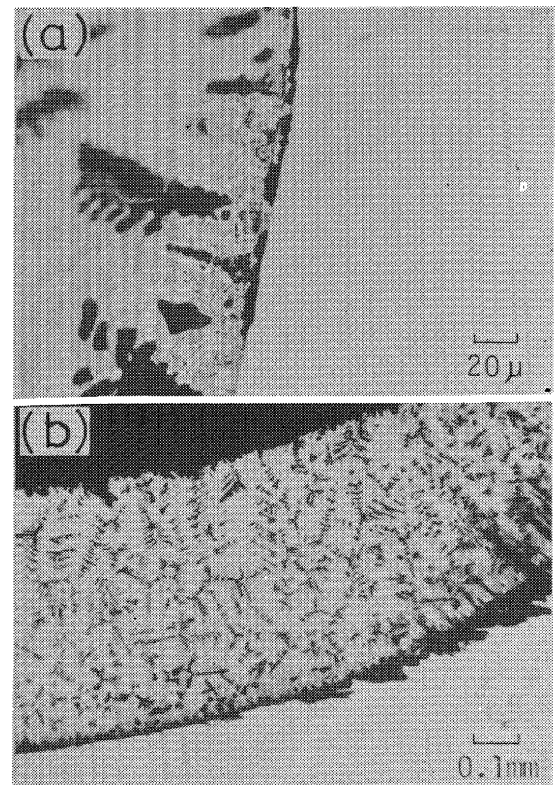


Photo. 3 Micrographs of corrosion of stainless steel/BAg-5 interface in B-2 (a) and B-3 (b) for 5 days.

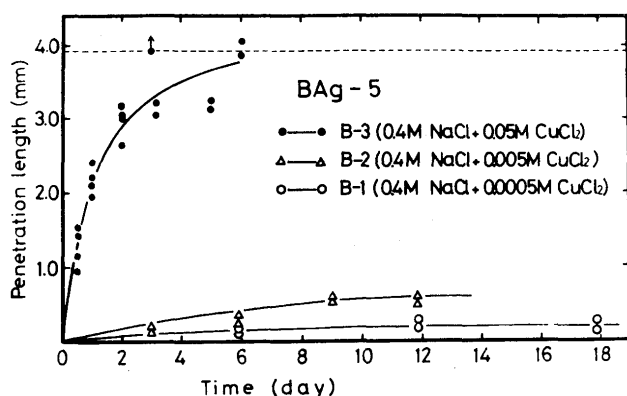


Fig. 5 Effect of copper content in corrosive solution on the penetration length (BAg-5/stainless steel).

tions for the specimens brazed with T-1 filler alloy. The scattering range is rather great compared with BAg-5 (Fig. 5) except B-1 solution in which the corrosion degree is small. Although the penetration length of the T-1/SUS 304 interface was shorter than that of the BAg-5/SUS 304 interface, the corrosion depth of T-1 filler alloy (dissolution depth of  $\alpha$ -Cu phase of T-1) was greatly larger than that of BAg-5 (Photo. 2).

To evaluate the corrosion resistance of various filler alloy/SUS 304 brazed specimens, immersion tests for 6 days were conducted in B-3 solutions, which enables rapid tests. The results are shown in Fig. 7. Interfacial corrosion of BAg-1a, 7 and T-3 penetrated through the whole interface of specimen. The corrosion depths of BAg-1a, 3 and T-1 ~ 4 were very severe and the corrosion depths exceeded 0.2 mm (mark: ●). On the other hand, those of BAg-4, 5 and 7 were less than 0.1 mm (⊕). Therefore, BAg-4 filler alloy is suitable for SUS 304 braze joint from the point of view of the corrosion resistance. The higher corrosion resistance of BAg-4 is brought by the nickel addition into the filler alloy. As nickel is preferentially distributed into  $\alpha$ -Cu phase, the selective dissolution of this phase is suppressed. The precise role of the additional elements against corrosion will be reported in the other paper.

#### 4.4 Effect of Copper Concentration in Corrosive Solutions on Corrosion

Both corrosion of filler alloy and interfacial corrosion were remarkably influenced by the copper concentration in corrosive solutions. Figure 8 shows the external polarization curves of T-1 filler alloy in A-1 and B-3 solutions. Natural electrode potential shifted about 100 mV toward the noble direction by the addition of 0.05 mol/l copper, however, anodic polarization curves were not so different. Meanwhile, the cathodic polarization curves show a typical diffusion control type<sup>5)</sup>, and the limiting current density

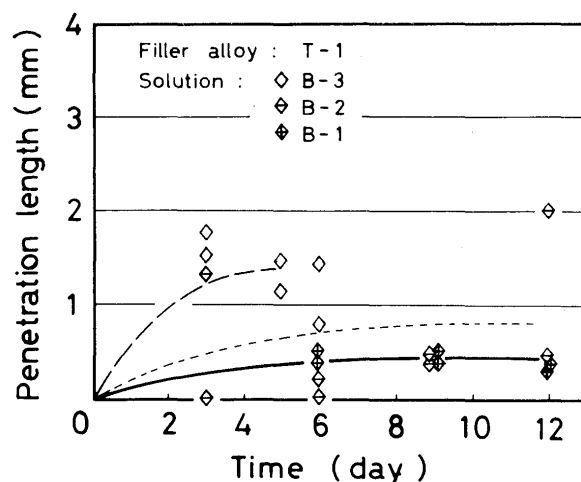


Fig. 6 Effect of copper content in corrosive solution on the penetration length (T-1/stainless steel).

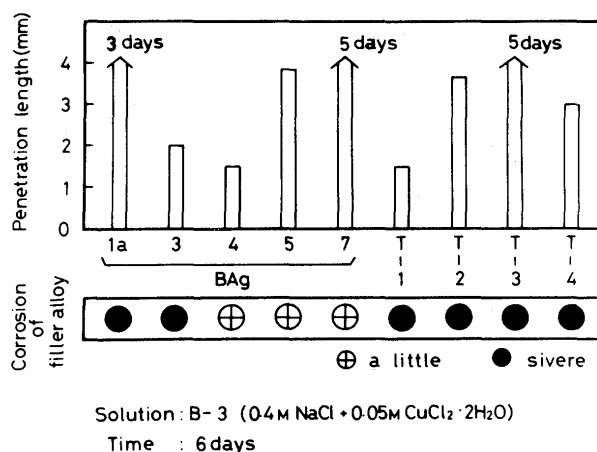


Fig. 7 Corrosion resistance of various filler alloys.

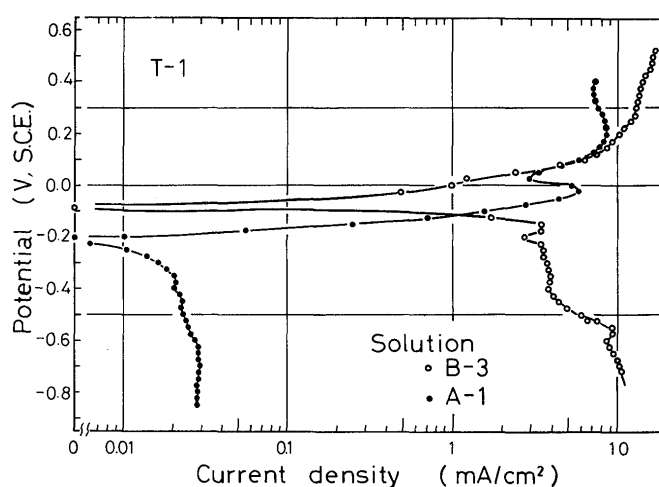


Fig. 8 Polarization curves of T-1.

widely increased by the existence of 0.05 mol/l copper. Similar polarization curves were obtained on the other filler alloys. Therefore, added copper to corrosive solution

enhances the cathodic reaction and this might be the main cause of the acceleration of corrosion in the solution of higher copper content.

The following discussions deal with the effect of copper concentration on the interfacial corrosion. As described in section 4.1, the stainless steel components were dissolved into the corrosive solution. Polarization measurement on stainless steel revealed that the natural electrode potential shifted to the noble direction and the anodic current density at same potential step was increased by the addition of copper in corrosive solution. But, in the range of more than 0.3 mV (S. C. E.), the slopes of these curves were not so different from each other. Cathodic polarization curves showed diffusion controlled type similar to that of the filler alloys, and the limiting current density in each solution was coincided well with that of the filler alloys. As the limiting current density was increased with the increase in cupric ion concentration in corrosive solutions, the corrosion reaction of this system is thought to be mainly controlled by the diffusion of cupric ions. Therefore, the cupric ions in the solution accelerate the anodic dissolution of stainless steel by the enhancement of cathodic reaction. This led the increase in the interfacial corrosion length of stainless steel.

#### 4.5 Corrosion Resistance of Used Silver Filler Alloys

In general, Ag-Cu-Zn ternary system filler alloys are consisted of  $\alpha$ -Cu phase,  $\alpha_1$ -Ag (Ag-Zn) phase and their eutectics<sup>6) ~ 8)</sup>. But the filler alloys containing Cd or In are consisted mainly of  $\alpha$ -Cu phase and Ag-Cd or Ag-In phase and eutectics, then the composition of silver solid solution is quite different from ternary alloys. This might decrease the corrosion resistance of the filler alloy containing Cd or In by causing the increase in the amount of zinc in  $\alpha$ -Cu phase or precipitation of  $\beta$  phase.

Kawakatsu<sup>2)</sup> measured the natural electrode potential of Ag-Cd and Ag-Zn alloys in 5% NaCl solution, and reported that the corrosion potential of both alloys shifts to base direction with the increase in the solute content. The electrode potential of Ag-Cd alloys were relatively more noble than that of Ag-Zn alloys<sup>2)</sup>. Therefore, the local galvanic corrosion of  $\alpha$ -Cu phase by the contact of Ag-Cd phase might be larger than the corrosion by the contact of Ag-Zn phase. If the electrode potential of Ag-In phase shifts similarly to Ag-Cd phase, the local corrosion reaction between  $\alpha$ -Cu phase and Ag-In phase may be enhanced, because the galvanic effect of Ag-In phase on the dissolution of  $\alpha$ -Cu phase might be expected larger than that of Ag-Zn phase, which leads the decrease in the corrosion resistance of the filler alloy containing indium.

#### 5. Conclusions

The following conclusions can be obtained by the immersion tests of silver brazed SUS 304 stainless steel in 0.4 mol/l NaCl solutions containing 0.05 mol/l cupric chloride.

- (1) The two corrosion types, the corrosion of filler alloy and the interfacial corrosion at filler alloy/SUS 304 brazed interface, are proceeded simultaneously. The corrosion of filler alloy is the preferential dissolution of  $\alpha$ -Cu phase and the interfacial corrosion is predominantly proceeded by the dissolution of stainless steel.
- (2) Both the corrosion of filler alloy and the interfacial corrosion are accelerated by the addition of cupric chloride in corrosive solutions. And the corrosion in preconcentrated copper solution is controlled mainly by the cathodic reaction.
- (3) Each main constituent of filler alloys and stainless steel except silver was dissolved into the corrosive solution.
- (4) Silver filler alloys containing Cd or In forms Ag-Cd or Ag-In solid solution phase and this seems to accelerate the corrosion of  $\alpha$ -Cu phase by galvanic effect and increasing the zinc content of  $\alpha$ -Cu phase.
- (5) The new type corrosion test specimen used in this study has no voids at brazed part, and is suitable for the measurement of the interfacial corrosion length.

#### Acknowledgement

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