



Title	H ₂ S Gas Corrosion Resistance of Copper Joints Brazed with Low Melting Temperature Copper Phosphorus Brazing Filler Metals(Mechanics, Strength & Structural Design)
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Citation	Transactions of JWRI. 1990, 19(2), p. 215-220
Version Type	VoR
URL	https://doi.org/10.18910/5647
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H₂S Gas Corrosion Resistance of Copper Joints Brazed with Low Melting Temperature Copper Phosphorus Brazing Filler Metals[†]

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Abstract

Copper joints were made by torch brazing or TIG brazing method using newly developed copper phosphorus brazing filler metals with low melting temperature and commercial BCuP-5. These joints were exposed in the corrosive atmosphere containing 100 ppm H₂S gas up to 1000 h. Degradation in strength and corrosion process of the brazed joints were investigated.

KEY WORDS: (Brazing) (Brazing Filler Metal) (Copper Alloys) (Low Melting Point) (Corrosion)

1. Introduction

New copper phosphorus brazing filler metals with low melting temperature which can be used at 650°C or lower were developed and the micro-structures of Cu-Ag-Sn-P quaternary filler metals¹⁾ and the effect of heat treatment or additional elements on brazability of the new brazing filler metals were also studied²⁾. The result indicated that the best composition in brazability was Ag/Cu(15/65)-3~3.5%P-15%Sn.

Copper phosphorus brazing filler metals are usually used to join copper or copper alloys in an air atmosphere without flux owing to fluxing action of phosphorus. Phosphorus bearing brazing filler metals were proved to be easily corroded in sulfur bearing gas atmosphere at high temperature³⁾. However, only qualitative comments on the corrosion behavior were given⁹⁾, and other literatures⁴⁾⁵⁾ tested the corrosion resistance in solutions containing sulfides,⁴⁾⁵⁾ but research under hydrogen sulfide atmosphere similar to the practical environment was rather few⁶⁾. The literature⁶⁾ concluded that the addition of zinc to Cu-P brazing filler metals improved the corrosion resistance in hydrogen sulfide atmosphere, but zinc loaded brazing filler metals can not be used without fluxing reagent.

On the other hand, Cu-Ag-Sn-P brazing filler metals developed by the authors¹⁾²⁾, can be used at 650°C or lower in air atmosphere without flux. In this study, the corrosion resistance of brazed copper base metal joints in H₂S gas atmosphere was evaluated using Cu-Ag-Sn-P low melting temperature filler metal and

BCuP-5, and the effect of brazing method was also studied on torch and TIG brazing.

2. Experimental Procedures

2.1 Braze specimen

The brazing filler metals tested in this experiment were Cu-15.3Ag-15Sn-3.5 P (BCuP-Sn) and Cu-15Ag-5P (BCuP-5). The melting temperature ranges and the brazing temperatures are shown in Table 1. The rod filler metals of 2.4 mm diameter were used. The brazing base metals were oxygen free high conductivity copper plate with the shape shown in Fig. 1(a). Torch brazing was processed using oxy-acetylene gas at the given temperature. TIG brazing was done to make the joint specimen under the conditions shown in Table 2. The brazing gap was fixed to 0.1 mm in both for torch and TIG brazing. The tensile strength of brazed specimens after corrosion test up to 1000 h were measured. The brazing base metal itself shown in Fig. 1(b) was also examined after the corrosion test in order to compare with the joint specimen.

2.2 H₂S gas corrosion test

As H₂S gas was highly corrosive, vinyl chloride was

Table 1 Chemical composition and melting point of filler metals

Filler metal	Element (wt%)				Melting point (°C)		Brazing temperature (°C)
	Cu	P	Ag	Sn	Solidus	Liquidus	
BCuP-Sn	bal	3.5	15.3	15	567	612	650
BCuP-5	bal	5	15		644	883	750

† Received on November 5, 1990

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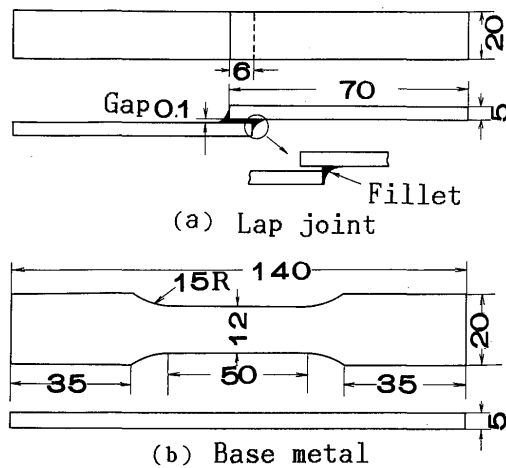


Fig. 1 Shape and size of corrosion test specimen.

Table 2 Condition of TIG brazing

Property of regular electrode on D.C.	D.C. bar(-)
Electrode	Tungsten(2.4 φ)
Current(A)	75~85
Ar flow rate(l/min)	7
Filler metal	BCuP-Sn, BCuP-5
Dia. of filler metal(mm)	2.4
Brazing speed(mm/min)	50

used to construct the corrosion test apparatus specially designed against H_2S gas attack. The gas concentration can be controlled at any level in the apparatus. The corrosion test temperature was $50^\circ C$, the relative humidity was 90%, and H_2S gas concentration was 100 ppm. H_2S gas was supplied through a gas container, and the quantities of air and H_2S were adjusted to make H_2S concentration 100 ppm before entering into the test chamber. The flow rate of air was kept constant to 10 l/min and the test was carried out up to 1000 h.

3. Results

3.1 Tensile strength of joints

The results of tensile test on the specimen brazed by torch brazing or by TIG brazing are shown in Fig. 2 and Fig. 3 respectively. In Fig. 2 all joints brazed with BCuP-5 were fractured in base metal until corrosion test for 50 h, but after 200 h exposure some specimens fractured at brazed part. After 500 h exposure, fracture in base metal was not observed and the all joints fractured at brazed part. Some of the joint specimens showed decrease in strength after 200 h tests, indicating the progress of corrosion. After 1000 h exposure, joint strength brazed with BCuP-5 decreased to about 50 kN, almost 1/4 of the initial value (about 200 kN).

Joints brazed with BCuP-Sn brazing filler metal

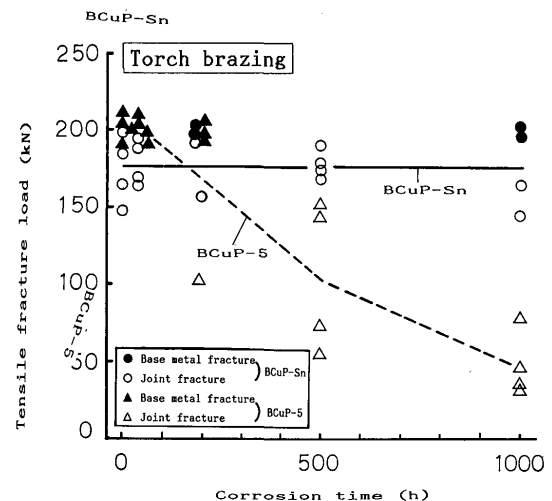


Fig. 2 Relationships between corrosion time and tensile fracture load of torch brazing specimens.

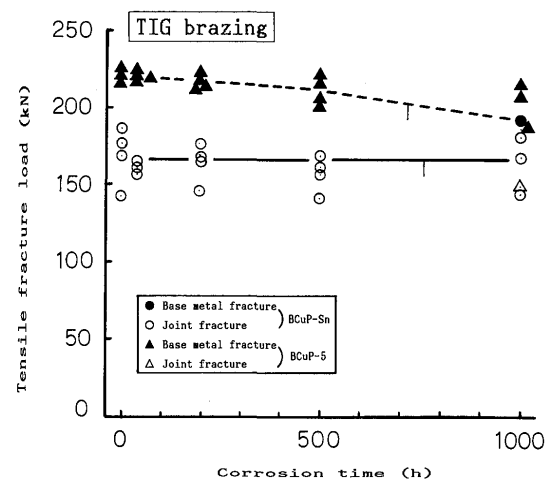


Fig. 3 Relationships between corrosion time and tensile fracture load with TIG brazing specimens.

showed no decrease in strength after 1000 h exposure. The appearance of fractured specimen after tensile test was also sound.

BCuP-Sn filler metal contains 15% Sn, and the phosphorus content is less than that of BCuP-5. This difference in composition was assumed to result in the improvement of corrosion resistance of the brazed part in H_2S gas atmosphere.

Figure 3 is the result of the tensile test after corrosion test up to 1000 h on the joints brazed by TIG brazing method. The all joints brazed with BCuP-5 were fractured in the base metals except one specimen exposed for 1000 h. Corrosion proceeded along the brazed parts in the specimen fractured at the brazed parts after 1000 h exposure. Even in the specimens fractured in the base metal after 1000 h exposure, considerable corrosion in the fillet was observed, however, the degree of corrosion in the fillet did not come up to effect the strength of the joints because the fillet size

was large. In further tests beyond 1000 h, decrease in strength would be expected as corrosion proceeds.

The strength of the specimen fractured in the base metal slightly decreased with the exposure time. The reason was assumed to be due to corrosion of the base metals. In fact, the corrosion of base metal itself gradually proceeded as shown in Fig. 4, though degradation rate in strength was comparatively low. Since a local corrosion cell would form between base metals and brazing filler metals under the relative humidity of 90%, corrosion of the brazed joints were accelerated than that of base metal itself.

The joints brazed with BCuP-Sn by TIG brazing the same behavior as those by torch brazing, namely no decrease in strength was observed after 1000 h exposure.

From the result of the tensile test mentioned above, the two characteristic items were pointed out. One is that the newly developed BCuP-Sn showed high corrosion resistance to H_2S gas irrespective of the brazing methods. The other is that the corrosion resistance of the commercially available BCup-5 is highly dependent on the brazing method, that is, the joints brazed by torch were severely attacked by H_2S gas, on the contrary those brazed by TIG brazing showed high corrosion resistance. The reason will be discussed in the following sections.

3.2 Microstructures

After corrosion test, the microstructures of the specimen were examined. The microstructures of corroded specimens brazed by torch were shown in Fig. 5 and Fig. 6. As shown in Fig. 5 the degree of corrosion in the fillet of BCuP-Sn was a little after 500 h and fair after 1000 h. Corrosion started at the front edges of the fillers in both cases. Corrosion proceeded only at front edges and the inner side was sound.

On the contrary, almost the whole fillers of BCuP-5 were corroded and the color of the surface was changed

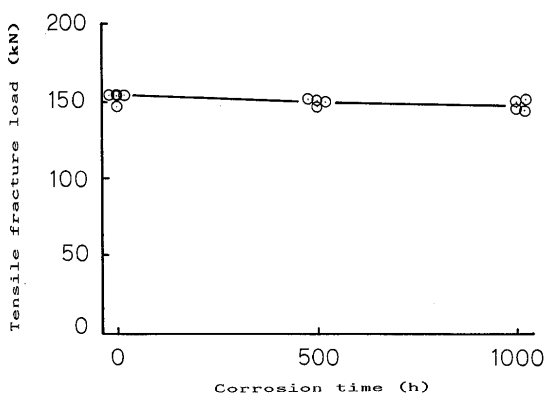


Fig. 4 Change of tensile fracture strength corrosion of copper base metal in H_2S gas atmosphere.

even after 500 h. After 1000 h exposure, the ratio of color changed portion increased. Corrosion from the surface of the fillets and the interface between copper base metal and brazing filler metal were observed. The corrosion from the surface was seemed to proceed into the brazed interface.

The difference in corrosion behavior between the two was assumed to be responsible to the difference in tensile strength. Here the decrease in strength was well corresponded to the ratio of corroded portion.

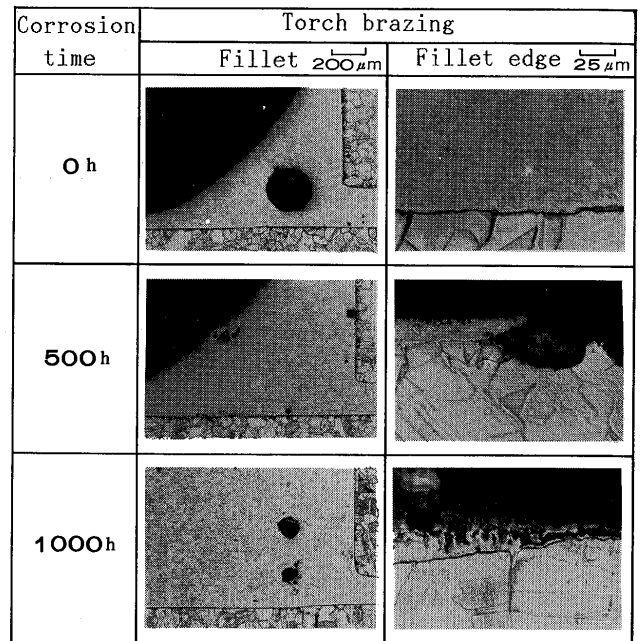


Fig. 5 Microstructure after corrosion of torch brazed joint, BCuP-Sn filler metal.

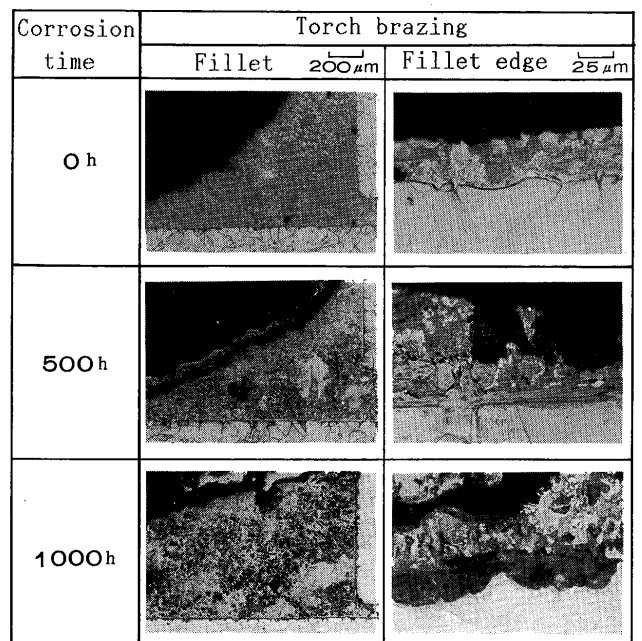


Fig. 6 Microstructure after corrosion of torch brazed joint, BCup-5 filler metal.

EPMA analysis was adopted to identify the corroded phase. BCuP-5 consisted of primary solid solution phase, $\text{Cu}(\alpha)$, and eutectic structure, $\text{Cu}(\alpha) + \text{Ag}(\alpha) + \text{Cu}_3\text{P}$, but the initiation phase for corrosion was not clear.

Corrosion from surface of the fillets might be the selective corrosion of $\text{Cu}(\alpha)$ phase, because Cu K α line was weak at $\text{Cu}(\alpha)$ phase in EPMA line analysis, and $\text{Cu}(\alpha)$, almost continuously crystallized along the copper base metal side of the interface between copper and filler metal, was corroded selectively. Even in the front edge of the fillet formed by BCuP-Sn the similar corrosion process was observed.

The microstructures of the corroded region of the fillets brazed by TIG are shown in Fig. 7. Even in the specimens exposed for 1000 h, only a little corrosion damage was observed in the fillets formed by both BCuP-Sn and BCuP-5. In the fillets of BCuP-5, the initiation of corrosion from the surface of the fillets and from the interface between copper base metal and brazing filler metal was observed to a mere extent.

The observed results were summarized as follows. A schematic of corrosion behavior was shown in Fig. 8. The measured corrosion lengths were summarized in Table 3. Corrosion length along the interface, l_I , was longer than the corrosion length from the surface of the fillets, l_F . Mark \odot means highly corrosion resistant, the lengths were less than 0.1 mm for interface and 0.2 mm for corrosion from surface respectively. Mark \times means highly sensitive to corrosion, the length were more than 0.5 mm for interface and 1 mm for corrosion from surface respectively.

BCuP-Sn filler metal showed good corrosion re-

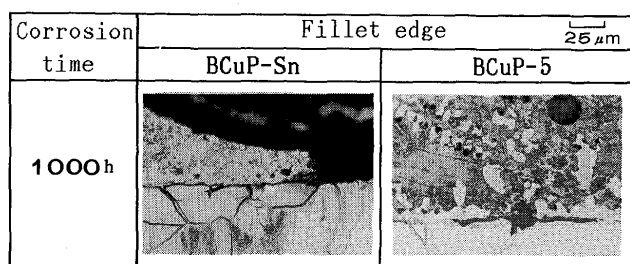


Fig. 7 The observation of corrosion at fillet edge on brazing joint.

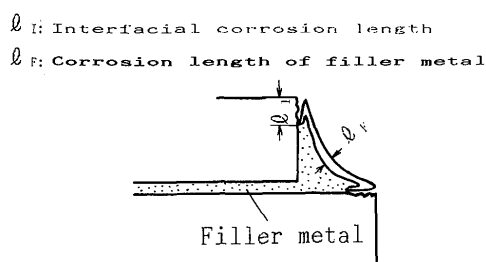


Fig. 8 Schematic illustration of corrosion.

Table 3 Corrosion length after H_2S gas corrosion tests

	BCuP-Sn				BCuP-5			
	500h		1000h		500h		1000h	
	l_F	l_I	l_F	l_I	l_F	l_I	l_F	l_I
Torch brazing	\odot	\odot	\odot	\odot	Δ	Δ	\times	\times
TIG brazing	\odot	\odot	\odot	\odot	\odot	\odot	\odot	\odot

l_F 0~0.1mm 0.1~0.3mm 0.3~0.5mm >0.5mm

\odot \circ Δ \times

l_I 0~0.2mm 0.2~0.6mm 0.6~1.0mm >1.0mm

distance to H_2S gas irrespective of the brazing methods. But the corrosion resistance of BCuP-5 brazed joints were extremely improved by TIG brazing. One reason of the improvement by TIG brazing was assumed that primary crystals $\text{Cu}(\alpha)$, likely to be corroded selectively, were finely distributed in the finely crystallized structure due to the fast cooling rate of TIG brazing. The effect of brazing method on corrosion resistance to H_2S gas was discussed in the following section.

4. Discussions

In torch brazing, oxy-acetylene flame was placed on copper base metals which would be uniformly heated to the temperature higher than the melting point of a brazing filler metal. When the base metal was heated up to the given temperature, the brazing filler metal was applied, and then the flame was turned off after the brazing gap (0.1 mm) was completely infiltrated by the filler metal.

In TIG brazing, arc generated between tungsten electrode and copper base metal heated instantaneously the part to be brazed. Heat was concentrated to the brazed part by a strong arc force.

Thus, there was much difference in heating process between torch brazing and TIG brazing method. TIG brazing has become popular recently in order to confine the annealed region a localized small part or in order to increase brazing speed. Cooling rates in torch brazing and TIG brazing are different with each other. Cooling rate in TIG brazing is faster than that in torch brazing. In this brazing experiment using BCuP-Sn filler metal, the cooling rates (at 650°C) were $180^\circ\text{C}/\text{min}$ in torch brazing and $335^\circ\text{C}/\text{min}$ in TIG brazing respectively. Cooling rates were $230^\circ\text{C}/\text{min}$ in torch brazing and $419^\circ\text{C}/\text{min}$ in TIG brazing of BCu-5 filler metal respectively, near the melting temperature (750°C) of the brazing filler metal. Microstructures of the fillets formed by the two different brazing methods are indicated in Fig. 9. In case of BCu-Sn, the microstructures were almost equal for both brazing method.

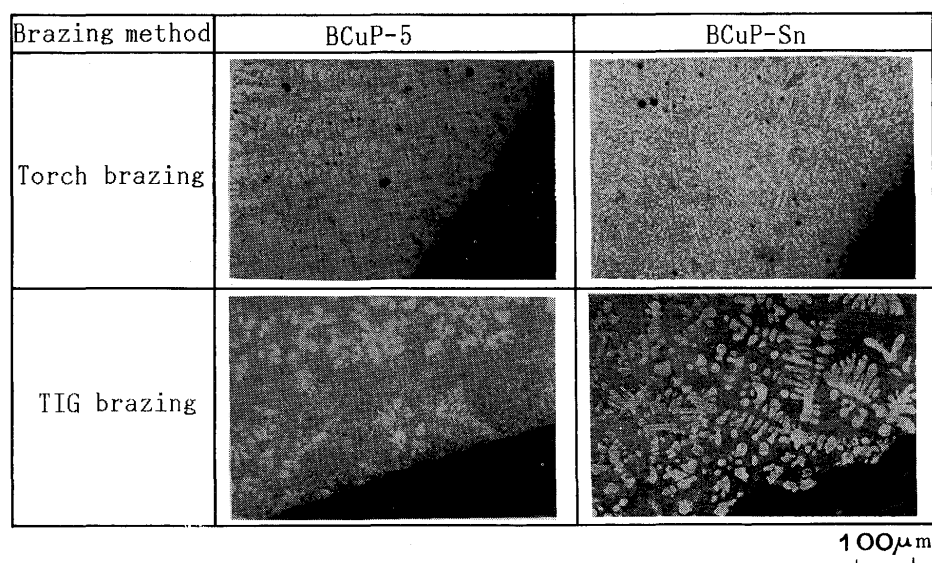


Fig. 9 Influence of brazing method on solidification structure (before corrosion test).

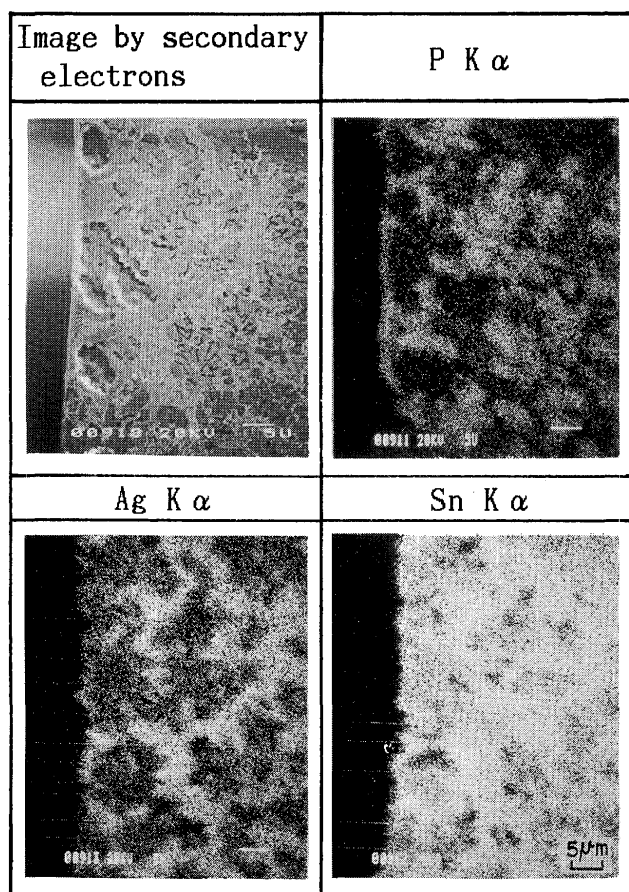


Fig. 10 EPMA analysis of torch brazed joint by BCuP-Sn filler metal (before corrosion test).

The results of EPMA analysis are shown in Fig. 10. The relatively large crystals were Cu(α) in which Sn, Ag, and P were dissolved as a solid solution. Quantity of crystallized Cu(α) was much more less than that in BCuP-5. Phosphorus enriched phase is Cu₃P and the residual P was distributed in Cu(α) solid solution. Sn

was distributed uniformly both in primary Cu(α) and in eutectic like structures. The primary solid solution phase Cu(α) in BCuP-5 contained Ag and P whereas in BCuP-Sn the phase contained Sn, Ag and P. It was assumed that the solution of tin into Cu(α) solid solution would enhance the corrosion resistance of BCuP-Sn.

On the other hand, BCuP-5 filler metal (Fig. 9) showed much difference in the microstructures depending on the difference in brazing method. Namely, grain size for torch brazing was large and that for TIG brazing was small. The result of EPMA analysis of the structures formed by the two different brazing methods are shown in Fig. 11. The difference in grain size of primary Cu(α) phase was definitely clear. The grain size of Cu(α) for TIG brazing was about 1/3 smaller than that for torch brazing. Obviously, the eutectic crystals around Cu(α) were also refined in TIG brazing. Cu(α) for both brazing methods contained Ag and P. The white phase around Cu(α) was a secondary crystallized Ag(α), and ternary eutectic was composed of Ag, Cu, and P. In spite of the difference in grain size, there was no difference in crystal structure.

After all, the reason why TIG brazed filler metal had high corrosion resistance to H₂S gas was summarized as follows:

- (1) separation of selectively corrosive phase, Cu(α), by refinement of eutectic like structures by its high cooling rate.
- (2) Refinement of primary crystal by rapid cooling.
- (3) Improvement of corrosion resistance by forced dissolution of Ag, Sn, and P super saturatedly into solid phases⁷⁾. A little inferiority of BCuP-5 to BCuP-Sn in TIG brazed joints was considered to be due to the difference in composition of solution elements in Cu(α),

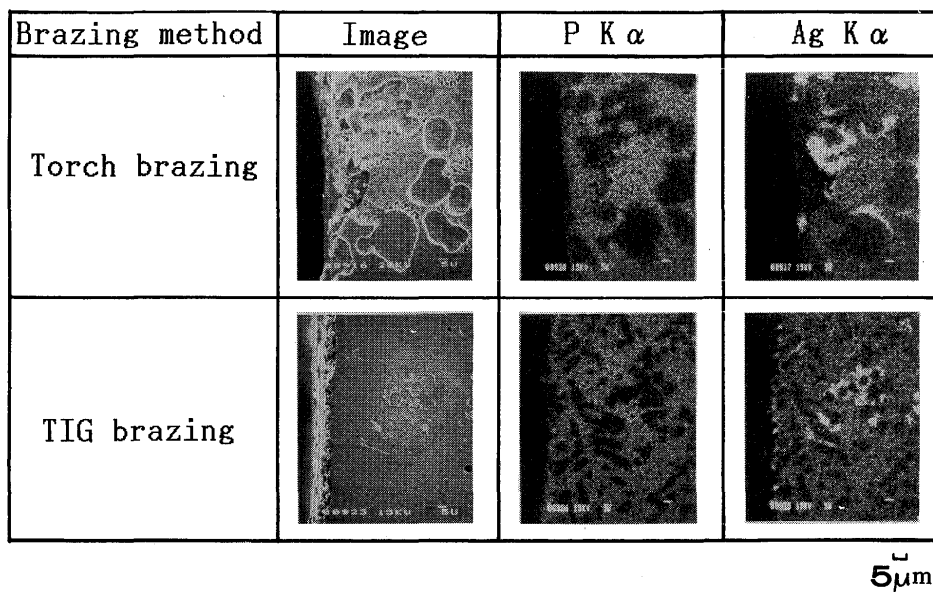


Fig. 11 EPMA analysis of BCU-P-5 filler metal brazed by different brazing method (before corrosion test).

silver and phosphorus for BCU-P-5, and tin, silver and phosphorus for BCU-P-Sn.

5. Conclusions

Using low melting temperature copper-phosphorus brazing filler metals, BCU-P-Sn and BCU-P-5 (specified by JIS), brazed copper lap joints were made and were exposed to H₂S gas atmosphere at 50°C, 90% RH, H₂S gas concentration of 100 ppm up to 1000 h. Strength and corrosion of the joints were observed after exposure.

The results are summarized as follows:

- (1) Strength of the joints brazed with BCU-P-Sn did not decrease after 1000 h exposure in H₂S gas atmosphere irrespective of brazing method.
- (2) Strength of the joints brazed with BCU-P-5 decreased to 1/4 of the initial values after 1000 h exposure when brazed by torch brazing method. But in TIG brazed joints, decrease in strength was negligible small even after 1000 h exposure
- (3) Two types of corrosion path, one from the surface of the brazing filler metal and the other from the interface of copper base metal and the brazing filler metal, were observed. Corrosion from the surface of the brazing filler metal was the preferential corrosion of solid solution Cu(α) phase. Interfacial corrosion mainly occurred in copper base metal near the interface suggesting the pre-

ferential corrosion of Cu(α) phase crystallized along brazed interface.

- (4) Improvement of corrosion resistance in H₂S gas of the joints brazed with BCU-P-5 by TIG brazing was due to the decrease in grain size of brazing filler metals to 1/3 of grain size as for torch brazing.
- (5) Superiority of BCU-P-Sn in corrosion resistance to BCU-P-5 was due to the difference in the composition of the primary crystal Cu(α), less crystallization of Cu(α), and small grain size of brazing fillet.

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