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Investigation on Corrosion Behaviour of Copper Brazed Joints

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Abstract

DHP (Deoxidized High Phosphorus) copper is widely used in various heat transfer units such as, air conditioners, refrigerators, evaporators and condensers. Copper sheets and tubes (ISODHP) were brazed with two different brazing alloys. Corrosion resistances of the joints were examined by polarization test. The selected fillers consisted of a silver-based brazing alloys (hard solder); AWS-BCu5, and a copper-based filler AWS BCuP2. All the joints were brazed utilizing two different brazing processes including furnace brazing under argon and air atmosphere. All of the fillers were used with and without flux. The microstructure of the brazed sheets was examined using both optical and scanning electron microscope (SEM). Hardness and leak tests were carried out on all the brazed tubes. In all brazing alloys selective and galvanic corrosion were observed in filler metals, but in copper phosphor alloys the copper adjacent to the joints were noticeably corroded by pitting method. It was found that the samples brazed with BAg5 filler metal using argon furnace show a higher resistance to corrosion. They also have a good ductility in the brazed zone.

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Keywords: Copper; Brazing; Corrosion.

1. Introduction

Copper is widely used in plumbing, heating, cooling, solar heating, air conditioning and fire sprinkler systems because of its favorable properties which include high thermal conductivity, high resistance to corrosion and easy processing, Karamiş et al. (2003). Brazing is widely used for joining copper alloys. The copper phosphide family of

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brazed metals is widely recommended for joining copper and high-copper alloys in a variety of applications, Sigler et al. (2007), particularly copper-to-copper tube including copper piping in cooling systems.

The resistant of joints to corrosion depends on many factors such as brazing condition including: temperature, atmosphere, time, flux type of filler metals and service condition.

The aim of this study is to investigate the corrosion resistance of two filler metals widely used in copper brazing.

2. Materials and Method

In this study, tubes and sheet made from ISO Cu-DHP (C12200) (phosphorus deoxidized non-arsenical copper, high phosphorus) were brazed together using different filler metals. These tubes were cold extruded. The tube had an outer diameter of 20mm and a wall thickness of 1.5 mm. The thickness of sheet was 1.5mm.The chemical compositions of the materials are given in table 1.Two different kinds of filler metal were used for brazing the copper tubes. The filler metals were AWS BCuP-5, and BCuP2and their chemical compositions are given in table 2. Brazing was performed using a tube furnace under two different atmospheres; air and argon. During brazing with flux, FB3-A flux dissolved in distilled water before applying to the filler.

Table 1. Chemicalcomposition of the copper.

	P	Mn	Pb	Al	Cu
Cu-DHP	0.0872	0.0804	0.00200	0.00888	Rem.

Table 2. Chemical composition of the filler metals.

Filler metal	Chemical composition (%)	Working temperature (◦C)	Melting range (◦C)
BCuP-2	P: 8, Cu: rem.	710	710–740
BCuP-5	Ag: 15, P: 6, Cu: rem.	710	650–800

Brazed assemblies were tested by applying a pressure of 7 bar. Metallographic samples were prepared by cutting them perpendicular to the brazed zone, mounted, polished and etched with 50% nital with 50%ferric chloride. Optical and scanning electron microscopy studies were done on the etched samples.

Brazed sheet was cut off and the cross sections of them were tested by polarization method. To investigate the corrosion properties of the samples, potentiodynamic testing was performed on 1cm_long samples in sea water(3.5%NaCl)at room temperature, using a potentiostat(model solartron SI 1287).Samples for corrosion testing were cleaned and rinsed in distilled water, and dried, Oh et al. (2002). The potential scanning rate was 0.5mV/s, the scanning rang was -800mV_500mV, platinum auxiliary electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. To evaluate the corrosion behavior of the joints, pitting potential and passive current density were measured using a cyclic anodic polarization test.

3. Results and discussion

3.1. Microstructural examinations

Microstructures of joints brazed with BCuP-2 are given in Fig. 1. As can be seen from the figure, round phosphorus poor dendrites in a matrix of Cu–P are observed. Dendrites have a uniform distribution in the matrix owing to proper brazing conditions, Zhang et al. (2010). Fig. 2. Shows the results of EDS analysis of the brazed samples and table 3 shows the chemical composition determined using EDS analysis of the tested samples after the brazing process.

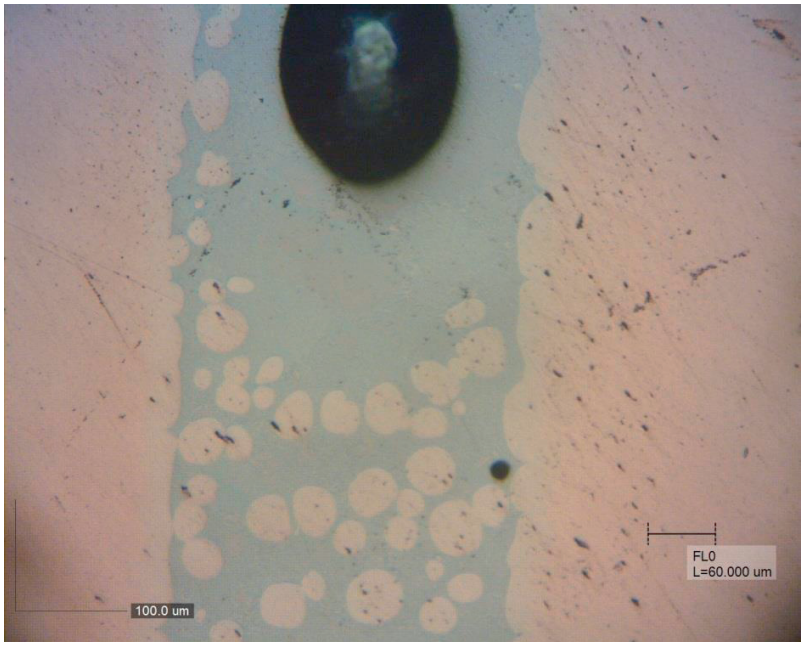

Fig. 1. Microstructure of the joints using BCuP2 filler metal.

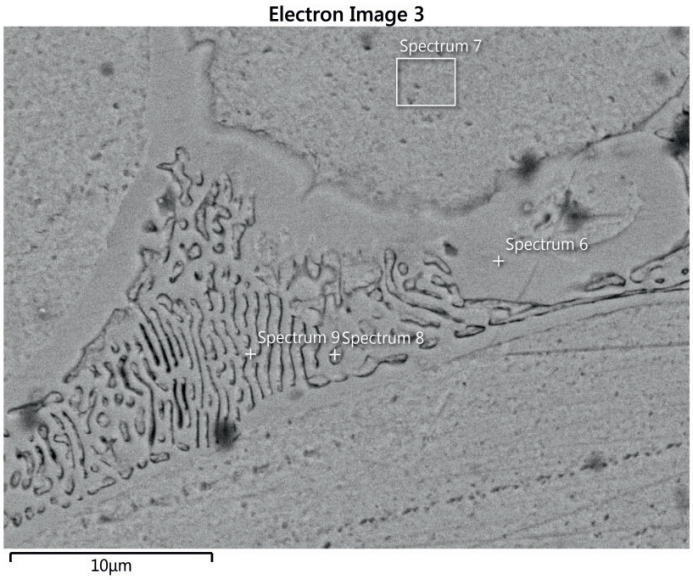

Fig. 2. Detailed microstructure of B-CuP2 filler metal.

Table 3. Chemical composition of the spots given in Fig. 2.

	Cu	P	O
Spec6	89.2	10.8	-
Spec7	95.9	2.6	1.5
Spec8	94.3	4.7	1

As shown in Fig. 3, BCuP-5 filler metal consists of three different regions. Regions in Fig. 4 are dendrites of copper solid solution (dark-gray 11), Ag–Cu–P eutectic (mottled-gray12) and silver rich dendrites around the eutectic (white10), respectively. Both copper solid solution and silver rich dendrites have irregular shapes, sizes and random orientations in the matrix. Fig. 4 shows thebraze layer with higher magnification and the area where EDS analysis was performed. Table 4 shows the chemical composition of the spots in Fig. 4. The silver rich dendrites have more silver content than the nominal chemical composition of the filler metal (i.e. 57.4%Ag in the dendrite).

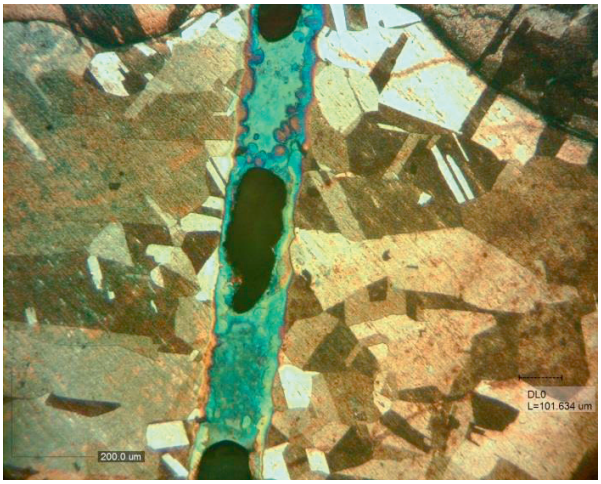

Fig. 3. Microstructure of the joints brazed with BCuP5 filler metal.

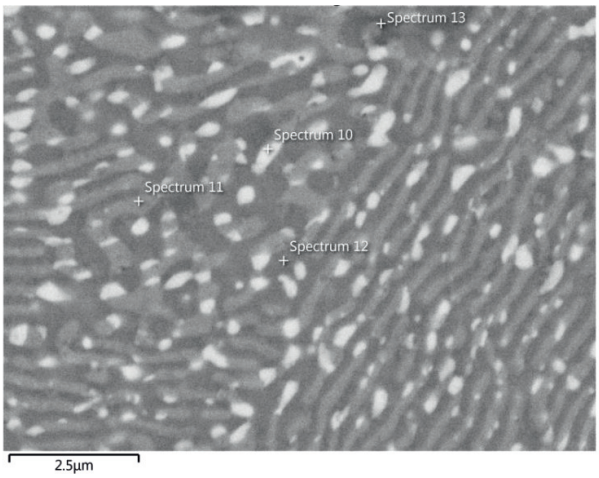

Fig. 4. Detailed microstructure of B-CuP5 filler metal.

Table 4. Chemical composition of the positions.

	Ag	Cu	P	O
Spec10	57.4	37.1	4.4	1.1
Spec11	5.6	89.6	4.2	0.6
Spec12	8.4	82.1	9.5	-
Spec13	11.9	77.8	9.2	1.1

Some discontinuities such as cavity and porosity can be seen within the joint area in Fig. 3.Incomplete brazing is frequently encountered in many brazed configurations. Generally, the reasons for these characteristics are narrow joint clearances, trapped gases, and/or improper filler metal selection.

The reasons for incomplete penetration of the filler into the joint gap using BCuP-5 filler metal are the slow flow property of the filler metal and improper fixing the joint assembly (Fig. 3). Another reason for slow flowing (sluggishness) is the wide melting temperature range of the filler metal (i.e. 650–800 ◦C).

Since the melting temperature range of BCuP-2 filler metal is narrow (i.e. 710–740◦C), it has a free flowing behavior and is capable of penetrating narrow joint gaps. Porosity is another frequently observed discontinuity defect in brazed joints. The reasons for porosity are the gases generated from vaporization of the constituents having lower melting temperature, gases produced by flammable materials present in the area to be brazed due to insufficient cleaning of the area or gas produced from some fluxes, Karamiş et al. (2003). Porosity has a high occurrence probability for slow flow filler metals because of the gases trapped in the molten filler metal. Porosity resulting from gases present in molten metal is shown in Fig. 1. Although the filler metal provides a sound bonding because of its free flowing and good wetting properties, porosities cannot be ignored in the samples brazed withBCuP-2 filler metal. Since this filler metal does not contain lower melting temperature alloy, these porosities arise as a result of insufficient cleaning or gases arise from fluxes. In brazing with BCuP-5 filler metal, there are much porosity. The reason for this is the high viscosity of the filler metal and insufficient cleaning of the brazed field also gases arise from fluxes (Fig. 4).

The phosphorus present is well able to cope with deoxidation during the brazing operation to permit good wetting and the formation of a sound bond, Dirnfeld et al. (1991). In addition, this filler metal has a relatively low price and high corrosion resistance.

3.2. Corrosion behavior

3.2.1. BCuP-2

Cyclic anodic polarization result of the samples brazed with BCuP-2 filler metal under argon and air with and without flux are presented in table 5.Compared with each other, argon environment without flux had the lowest current density(4.57E-10A.Cm^-2),also pitting no observed in the curves. Corrosion resistance of this filler metal was decreased by using flux also, brazing in air reduced corrosion resistance, Valero-Gómez et al. (2006) Moreover, copper joints brazed with BCuP-2 filler metal in air with flux show pitting that cause the joints to be de-bonded rapidly.

3.2.2. BCuP-5

Cyclic anodic polarization results of samples brazed with BCuP-5 filler metal under argon and air with and without flux are shown in table 5. Compared with each other, brazed joints in argon without flux show less current density (4.24E-10A.Cm^-2), but in air environment with flux current density increases. Moreover, pitting is observed in the curves.

3.2.3. Comparison of filler metals

As can be seen from table 5, the lowest content of current density is for BCuP-5 in argon without flux (4.23E-10A.Cm^-2). This is for three reasons:

- Fluxes were used in copper brazing have corrosive media. Therefore, flux residue create corrosive environment and increase the rate of corrosion as well which causes pitting.
- Brazing in air environment produces copper oxide in grain boundaries of the filler metal and decreases corrosion resistance.
- BCuP-5 filler metals contain 15%Ag that produce Ag.Cu.P eutectic and Ag solid solution in microstructure that they are nobler than Cu_3P or Cu solid solution. Therefore, this filler metal showed better corrosion resistance than BCuP-2 filler metal.

Table 5. Corrosion and pitting results for different brazing conditions.

Test-Number	Filler Metal	Atmosphere	Temperature	Time	Flux usage	Attempt	i_{cor}	Pitting
B.CuP5							7E-10	No
1	B.CuP5	Air	710 C	10 min	No	Yes	7.45E-10	No
2	B.CuP5	Air	710 C	10 min	Yes	Yes	26.8E-10	Yes
3	B.CuP5	Ar	710 C	10 min	No	Yes	4.238E-10	No
4	B.CuP5	Ar	710 C	10 min	Yes	Yes	4.84E-10	No
B.CuP2							13.524E-10	No
7	B.CuP2	Air	710 C	10 min	No	Yes	14.624E-10	No
8	B.CuP2	Air	710 C	10 min	Yes	Yes	5.5942E-10	Yes
11	B.CuP2	Ar	740C	10 min	No	Yes	4.572E-10	No
12	B.CuP2	Ar	740 C	10 min	Yes	Yes	5.8321E-10	No
Cu-DHP							5.6913E-10	Yes

The brazed assemblies using these filler metals were tested for leaks under a pressure of 7bar. Water leakage observed in the samples brazed with BCuP-5 filler using flux in air. Finally, the higher the silver content, the lower the hardness of the brazed area. Presence of phosphorus relatively increases hardness. For example, the hardness of joint area was measured to be around 100 HV for the samples brazed with BCuP-2 and around 71 HV for the samples brazed with BCuP-5 filler metal.

4. Conclusion

- The samples brazed with BCuP-5 filler metal under argon atmosphere and without using flux represented the highest corrosion resistance in sea water.
- Flux residue create corrosive environment. Therefore, cleaning flux is an important factor in corrosion reduction.
- The hardness of the brazed area varies depending on its chemical composition. The higher the silver content, the lower the hardness of this area. The presence of phosphorus increases the hardness.
- When the filler metal has free flowing and good wetting properties, generally porosities can be avoided. Insufficient cleaningthe surfaces to be joined and also the gases that produce from fluxes can led to formation of porosities within the braze layer.

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