Effect of Temperature on Corrosion behavior of Copper Silver Phosphorus Brazing Alloys in Chloride Containing Solution

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Abstract. The groups of phosphorus-containing brazing alloys are the most favored filler metals used for joining copper and copper-base alloys. These brazing alloys are expected to have the optimum corrosion resistance during the application. However, failures arise at the braze joint generally caused and initiated by the corrosion of the brazing alloys when used at higher temperature than the room temperature. Since most studies of the phosphorus containing brazing alloys were performed at room temperature, this work has been extended to investigate the effect of various temperature on the corrosion behavior. Electrochemical measurements were carried out to observed the temperature effect with the temperature variation of 25, 40, 55 and 70 °C in 3.5% NaCl electrolyte. As the results, the copper-silver-phosphorus brazing alloy was undergone a selective dissolution by the attack of Cl- to the copper element. The temperature dependence of the alloy showed in agreement with the relationship of 2.3RT/F that have similar manner on pure copper tafel region. The schematic diagrams of the corrosion process were then proposed. This work could be helpful to understand in the field practically because the application temperature is usually higher than that of room temperature in general.

Keywords: Brazing alloy, corrosion, high temperature corrosion

1. Introduction

The families of phosphorus-containing brazing alloys are the most favored when copper and copper-base alloys are brazed [1,2]. During the brazing process, phosphorus reacts when the alloys melts, producing copper metaphosphate slag. This feature is known as a self-fluxing function, therefore, usual fluxes may be omitted when phosphorus-containing brazing alloys are used for joining copper and copper base alloys. Moreover, the higher phosphorus content, generally with the maximum of 8.25 wt%, the better the alloy flowing into the joint gap.

Silver addition to a phosphorus-containing brazing alloy is well known not only improving its flow characteristic, but also increasing its ductility. Better properties in ductility possibly gained at the equal flow characteristic of the silver-free brazing alloy [3,4].

The phosphorus-containing brazing alloys with silver addition corrosion behaviour was studied by Valero-Gomez et al.[5] in lithium bromide solution at 25°C. The passive layer of the alloys was formed. The passive region showed a large range of inhibition even though the cracked layer were observed and occured from its started to form. Furthermore, copper-
silver-phosphorus alloys were proved to have more noble potential in lithium bromide solution than the silver-free alloys. It also has been established that phosphorus-containing brazing alloys with silver addition formed a protective passive film on the surface of the alloys when exposed to water. Idrissi et al.[6] found that the film mainly made of cuprous oxide and calcium carbonate when studied the corrosion behaviour of the alloy in local water at room temperature.

Besides its excellences as a corrosion resistant, some failures of the brazed joint were often arisen. Sigler et al. [7] reported a failure in welding transformers that brazed with copper-silver-phosphorus brazing alloy. The water leaks of failed transformers were caused by the mechanism of sulfide-induce corrosion. Selective dissolution of copper was observed and postulated occurred by the attack of sulfide species initiated at the braze alloy. The cavity became larger due to the catalyzed attack of copper either in the braze or in the base material by the phosphoric acid that produced from the changes of water chemistry under the corrosion product of copper sulfide.

Furthermore, a leak in the clip-to-strand braze connection that initiated in the braze alloy has been reported by Joseph A. Worden et al. [8]. In the report, the corrosion mechanisms were proposed into two stages. At the first stage, the brazing alloy was attacked by the water, particularly at the phosphorus rich phase of the alloy. The existing voids at the brazing alloys give the opportunity for water to stagnate and initiated the corrosion. Afterwards, this void grows as the corrosion progresses. At the second stage, the corrosion of the void penetrates until reaches the copper as the base metal. Hence, the phosphoric acid that produced by the corrosion of the brazing alloy attacked the copper trough the void.

The copper-silver-phosphorus brazing alloys have much attention as consequences of some good properties when used for joining. However, the failures arise frequent at the braze joint. The failures are generally caused and initiated by the corrosion of the brazing alloys. Copper as the base material has been getting a large attention for their corrosion behaviour. Yet, less comprehensive information available for the corrosion behaviour of the brazing alloys, particularly in the chloride containing electrolyte.

The present study was intended to observed the behaviour of the copper-silver-phosphorus brazing alloy exposed in the 3.5% NaCl solution. In addition, since most studies of the phosphorus containing brazing alloys have been made at room temperature, this work was performed to study the temperature effect of copper-silver-phosphorus brazing alloy corrosion with temperature at 25, 40, 55 and 70°C. This work could be helpful to understand in the field practically because the application temperature is usually higher than that of room temperature in general.

2. Experimental Procedures

The materials used was commercial copper-silver-phosphorus brazing alloy with composition of 85% Cu, 15% Ag, 5% P, the materials were made with the exposed area approximately 1cm². The pure Copper of 99% purity was also utilized to compare the corrosion behavior. All the materials were supported by Doosan Heavy Industries & Construction Ltd. Prior each experiment the materials were mechanically polished successively with SiC abrasion paper from 600 to 2000 grits, and then mirror finished using Buehler polishing cloth wetted with diamond suspension sequentially from 9 to 1 µm. After polishing the materials were cleaned by ultrasonically degrease the coupon for 5 minutes in methanol or ethanol, and then rinse thoroughly in distilled water before dried.
The electrochemical data acquisition equipment was Princeton Applied Research potentiostat model 273A controlled with PowerSuite software, and the reference electrode used was silver/silver chloride (Ag/AgCl saturated KCl).

The experiments were conducted using three-electrode cell with a platinum mesh as the counter electrode adjacent to the working electrode (brazing alloy and copper). The condition was in open air atmosphere under 3.5% NaCl electrolyte. The electrolyte solution was prepared by using distilled water and analytical grade NaCl. The potentiodynamic experiments of the brazing alloy were performed at scanned potential from -0.1 mV\textsubscript{SSCE} vs OCP to 0.4 V\textsubscript{SSCE} with the scan rate of 0.1 mV/s at 25, 40, 55 and 70°C.

Cyclic voltammetry experiments were carried out with copper and brazing alloy at 25°C and the cyclic voltammograms were recorded starting from -0.8 mV\textsubscript{SSCE} and reversed when reaching 1 V\textsubscript{SSCE} back to the starting point at the scan rates of 10, 20, 30, and 40 mV/s.

Potentiostatic polarization experiments were performed on active-passive transition region potential of the brazing alloy that obtained from the potentiodynamic polarization curve. The corrosion behaviour of the alloy was evaluated by statically polarized the materials at each temperature of 25, 40, 55 and 70°C for 3600 s.

The corrosion products at each temperature resulted from the potentiostatic polarization experiments were identified by XRD examination. The morphologies of the corroded samples were analyzed by optical microscope and scanning electron microscopy (SEM, Hitachi S-4100).

### 3. Results

#### 3.1. Potentiodynamic polarization

The potentiodynamic polarization of the copper-silver-phosphorus brazing alloys in 3.5% NaCl solution resulted in E vs log i curves and represented in figure 1.

![Figure 1](image)

**Figure 1.** Potentiodynamic polarization curve of copper-silver-phosphorus brazing alloys in 3.5% NaCl solution at various temperature.

Tafel slope method were used to obtain the corrosion potential and corrosion current of the alloy. The corrosion potential ($E_{corr}$) shifted towards more negative value with respect to the increased of temperature and the corrosion current was also increased regarding to the increased of temperature. Moreover, the anodic tafel slopes were followed the changes of the temperature, at higher temperature the slope was steeper than that of lower temperature. The
corrosion properties of the alloy that obtained by tafel slope method were summarized in table 1.

Table 1. Copper-silver-phosphorus electrochemical parameters obtained from tafel slope method

| T (°C) | \( E_{\text{corr}} \) (VSSCE) | \( I_{\text{corr}} \) (A) | \( \eta_a \) (mV/dec) | \( \eta_c \) (mV/dec) |
|--------|-----------------------------|-------------------------|----------------|----------------|
| 25     | -0.149                      | 9.036x10^{-7}           | 58             | 76             |
| 40     | -0.154                      | 2.8x10^{-6}             | 61             | 66             |
| 55     | -0.156                      | 7.43x10^{-6}            | 70             | 57             |
| 70     | -0.164                      | 2.01x10^{-5}            | 73             | 68             |

The peak current obviously appeared in of the potentiodynamic polarization curve at 25°C. This peak has appeared up to 40°C with increased in current value as the temperature increased. While, the potentials were relatively unchanged. Further polarization above the peak current potential produced region with decreasing in current until touched the minimum current value. Subsequently, the current rapidly increasing until followed by a current plateau at the limiting current region.

3.2. Cyclic voltammetry

Cyclic voltammetry experiments were conducted at the scan rate varied from 10 mVs\(^{-1}\), continued to 20 mVs\(^{-1}\), 30 mVs\(^{-1}\) and up to 40 mVs\(^{-1}\). The experiments resulted voltammograms of copper and copper-silver-phosphorus brazing alloys that exposed to the solution contained Cl\(^-\) in an open air atmosphere. At the anodic region of copper voltammogram two peaks were showed in each scan rate, noted as A1, and A2 in figure 2. The A2 peak appeared like a shoulder at the small scan rate, then gradually more apparent with increasing scan rate. When the scan rate reached 40 mVs\(^{-1}\), both of the anodic peaks almost have the same current intensity. Instead of the A2 peak, the A1 peak was obvious in any scan rate. Moreover, both of the anodic peak shifted towards positive values with increasing scan rate.

![Cyclic voltammograms of Copper in 3.5% NaCl electrolyte at 25°C with the scan rates of 10, 20, 30, 40 mV/s, b) Copper anodic peak current versus square root of scan rate.](image)
The cathodic peak of copper voltammogram, noted as C in the figure 2a, was obviously appeared at any scan rate. The peak increasing in current value with increasing scan rate. Linear dependence of $I_a$ on the $v^{1/2}$ obtained by cyclic voltammetry were showed in figure 2b. All copper's cyclic voltammetry parameters are presented in table 2.

### Table 2. Cyclic voltammetry anodic-cathodic peak of Copper in 3.5% NaCl solution at 25°C

| Scan Rate (mV/sec) | $E_{a1}$ Peak (V vs. SSCE) | $E_{a2}$ Peak (V vs. SSCE) | $E_c$ Peak (V vs. SSCE) | $I_{a1}$ Peak (A) | $I_{a2}$ Peak (A) | $I_{c}$ Peak (A) |
|-------------------|---------------------------|---------------------------|------------------------|------------------|------------------|-----------------|
| 10 mV/sec         | 0.335826                  | 0.45251                   | -0.208297              | 0.01957          | 0.01151          | -0.01191        |
| 20 mV/sec         | 0.466369                  | 0.652792                  | -0.371896              | 0.0201           | 0.0199           | -0.01745        |
| 30 mV/sec         | 0.429262                  | 0.634639                  | -0.358017              | 0.0246           | 0.0239           | -0.0232         |
| 40 mV/sec         | 0.518960                  | 0.688710                  | -0.460460              | 0.0343           | 0.0328           | -0.0331         |

The voltamograms of copper-silver-phosphorus brazing alloy were shown with the potential value of cathodic peak in the range of copper's voltammograms potential and depicted in figure 3a. The anodic peaks were seen consisted of two peaks agreed with the typical manner with copper's voltammograms, unless the peak at higher potential poorly showed and more like shoulder than a peak.

### Figure 3.

a) Cyclic voltammograms of Copper-silver-phosphorus brazing alloy in 3.5% NaCl electrolyte at 25°C with the scan rates of 10, 20, 30, 40 mV/s, b) Copper-silver-phosphorus brazing alloy anodic peak current versus square root of scan rate.

The dependence of $E_a$ and $I_a$ on the $v^{1/2}$ of the alloy were evaluated, plots in figure 3b showed a high degree of linearity. All the cyclic voltammetry parameters of copper-silver-phosphorus brazing alloy are presented in table 3.

### Table 3. Cyclic voltammetry anodic-cathodic peak of Copper-silver-phosphorus brazing alloy in 3.5% NaCl solution at 25°C

| Scan Rate (mV/sec) | $E_a$ Peak (V vs. SSCE) | $E_c$ Peak (V vs. SSCE) | $I_a$ Peak (A) | $I_c$ Peak (A) |
|-------------------|------------------------|------------------------|----------------|----------------|
| 10 mV/s           | 0.4130                 | -0.2907                | 0.0207         | -0.0182        |
| 20 mV/s           | 0.4765                 | -0.3792                | 0.0261         | -0.0253        |
| 30 mV/s           | 0.5367                 | -0.4887                | 0.0311         | -0.0340        |
| 40 mV/s           | 0.5792                 | -0.5417                | 0.0344         | -0.0378        |
3.3. Potentiostatic polarization

The active-passive transition of the copper-silver-phosphorus brazing alloy were tried to evaluate by potentiostatic polarization at each temperature of 25, 40, 55, and 70°C. The potential of the active-passive transition region that chosen was 250 mV \(_{\text{SSCE}}\). The curves in figure 4 represented that the current resulted become greater with increasing temperature. The current curve at 70°C showed some abruption as the consequences of less stability of the corrosion product on the surface, meanwhile the curve at 25°C showed the highest degree of its stability.

![Figure 4. Potentiostatic polarization of Copper-silver-phosphorus brazing alloy with the potential of 250 mV in 3.5% NaCl at 25, 40, 55, and 70°C.](image)

3.4. Characterization

X-ray diffraction was used to characterize the corrosion product that produced on the surface of the copper-silver-phosphorus brazing alloy as the result of potentiostatic polarization. In addition, the untested brazing alloy was observed to obtain the origin of the peak. The X-ray diffraction pattern of the corrosion product are summarized in figure 5. The Cu, Ag, and Cu₃P were identified as the main elements of the brazing alloy. When the alloy exposed to 3.5% NaCl at 25°C the existence of CuCl were confirmed. Indeed, the CuCl were found in each of the temperature. The higher the temperature the corrosion worsened and started to dissolving more element, hence the AgCl were detected at 55 and 70°C. In addition, the CuCl were further appeared in each varied time when statically polarized.

![Figure 5. X-ray diffraction pattern of the corrosion product.](image)
Figure 5. XRD examination of Copper-silver-phosphorus brazing alloys, a) untested, b) at 25°C, c) at 40°C, d) at 55°C, and e) at 70°C.

SEM and EDS examination were done to analyze the corroded area in the microscopic scale. Figure 6 showed SEM micrographs of the four brazing alloys based on the time of measurements. The quality of the corroded area observed were deteriorating with the increasing of temperature.

Figure 6. SEM images of the alloys’ cross section with 1000x mag. after potentiostatic polarization at 250 mV(SSCE) in 3.5% NaCl solution at various temperature: a) 25°C; b) 40°C; c) 55°C; d) 70°C.
4. Discussion

4.1. Electrochemical corrosion behavior

The anodic region of the alloy potentiodynamic curves showed the typical anodic behaviour of pure copper in chloride containing electrolyte [9-16]. The alloy anodic curves can be divided into three sections as shown in figure 1: the first section is the apparent tafel region. The second section is where the peak and minimum current appeared. The last section is where the limiting current region existed.

At the apparent tafel region in 25°C potentiodynamic curve, the anodic slope was 58 mV/decade. P. A. Lush and M. J. Carr [18] proposed that at low current density with the tafel slope close to 60 mV/decade for the pure copper in chloride containing electrolyte the dissolution was mass-transfer controlled. Hence, the dissolution of the alloy might have the similar manner. However, at high current density the tafel slope of the alloy change to close to 120 mV/decade. It was believed that the steep slope at high anodic current density may influenced by the existence of film on the surface caused the limited diffusion of the reacting species. Previous studies have reported such behavior on covered copper with porous film on the surface [18,19].

The anodic dissolution behaviour of pure copper in chloride containing electrolyte has been studied comprehensively by some authors [9-11, 14-16]. The dissolution of copper by the attack of Cl- was believed initiated with the adsorption of Cl- ions on copper surface and formed submonolayer of Cl adatoms that shielded the surface [15]. The dissolution was then continued with the formation of CuCl and/or CuCl2- corrosion product. H. Lal and H. R. Thirsk [17] have suggested that the CuCl2- were the limited diffusion species to the solution and CuCl were precipitated on the surface. The voltammograms of the alloy (figure 3) showed the first peak at the lower potential that corresponds to the precipitation of CuCl. The second peaks of the alloys voltammograms, unlike the copper (figure 2) as described by D. Tromans and Ru-hong Sun [11], the peaks were more like a shoulder. This shows that the rate of the dissolution of the alloy through CuCl2- is more undesireable than in the pure copper. The relationship between Ia on the √ν suggested that the anodic reaction was mainly diffusion controlled with the limiting diffusion species is CuCl2-. The alloy’s nature of microstructure was believed to be the main cause of the limited mass-transport processes. Since the dissolution occurred by selective attack of copper element in the alloy, the other elements inhibit the corrosion product dissolved to the solution.

In compliance with the cyclic voltammetry behavior, at the active-passive region of the 25°C potentiodynamic curve, the peak current at the minimum current density was contributed by the formation of CuCl that covered the surface. As the potential shifted to the more positive value the current density observed increased once again, this anodic behaviour was associated with a strong role of the CuCl2- dissolution from the surface to the bulk solution.

4.2. The effect of temperature

The apparent tafel slopes were in agreement with the relationship of 2.3RT/F as firstly introduced by Lal and Thirsk [17] for pure copper in chloride containing electrolyte. Lee and Nobe [13] offered the similar relationship which indicate that in the apparent tafel region electrodissolution of Cu controlled by mixed mass-transfer and charge-transfer. The alloy tafel slopes behaviour dependencies to the temperature with such relationship of 2.3RT/F showed by the tendency of the Ecorr and the anodic slope that follow the changes of the temperature. Shifted to more negative potential, and at higher temperature the slope was steeper than that of lower temperature.

The appearances of active-passive region were also gradually vanished as the temperature increased. The formation of CuCl is faster than the formation of CuCl2- at lower
temperature of 25°C and 40°C, thus the surface have a high possibility to be covered by precipitated CuCl that change the slope and obviously decreasing the current density. On the other hand, at higher temperature of 55°C and 70°C, the temperature not only improving the rate of the CuCl₂ formation but also faster the mass-transport of CuCl₂ limited diffusion species to the solution. These circumstances make the CuCl cannot inhibit the corrosion process.

D. Starosvetsky et al. [15] reported on their work that the anodic behaviour of the active-passive region was a function of the passivity breakdown process that associated with incubation period. In the similar approach, the alloys were statically polarized in the anodic potential of 250 mV_{SSCE} at each temperature. Static polarization curve showed that the incubation period decreasing with temperature increased. In agreement with the result of D. Starosvetsky et al. the activation was stimulated by either with the applied potential or the temperature. The incubation period seems to decrease with increasing temperature or increase in applied potential, and almost directly activated for dissolution at higher potential or temperature. Similar manner of the incubation period was shown by the iron and steels, and agreed that this feature is the initial stage of pit nucleation [15]. The surface characterization of the alloys after potentiostatic experiments showed the tendency of pitting to occur become higher with increasing temperature. Some abruptions were also found in the potentiostatic curve at 70°C.

This incubation period time was observed at different time statically polarized the alloy at the same potential of 250 mV_{SSCE}. The existence of the CuCl salt layer was identified at each varied times and temperature by the XRD SEM and optical microscope examination showed that the layer was in the form of selective dissolution region and this region increased in the depth of the attacked region with time and temperature. This feature suggested that the alloy was in the active state at the potential of 250 mV_{SSCE} as either at the incubation period time. From the electrochemical measurements, the schematic drawing proposed as in figure 7.

![Figure 7](image_url)

**Figure 7.** Schematic diagrams of Copper-Silver-Phosphorous Brazing Alloy for electrochemical corrosion with the effect of temperature.

5. **Conclusion**

The copper-silver-phosphorus brazing alloy was undergone a selective dissolution by the attack of Cl⁻ to the copper element. The anodic behaviour of the alloy showed the typical manner of the pure copper anodic behaviour. The temperature dependence of the alloy showed in agreement with the relationship of 2.3RT/F that have similar manner on pure copper tafel region. The increasing of the slopes was more due to disturbed in balance between the charge-transfer and mass-transfer control. The temperature effect have similar role with the applied potential, which is the higher both applied, the easier the copper and brazing alloys activated. The morphologies of the corroded area of the alloy informed that the
typical characteristic of pitting nucleation by the presence of incubation period were in a good agreement.

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