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To cite this article: A Nurrochman et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 526 012033

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Evaluation of silver-copper-tin brazing alloy corrosion behavior in chloride containing electrolyte at various temperature

A Nurrochman¹,²,*§, E Prajetelistia³,§, K Cho⁴

¹ Mining Engineering Department, Universitas Islam Bandung, Bandung, Indonesia
² Mechanical Engineering Department, STT Mandala, Bandung, Indonesia
³ Materials Science and Engineering Department, Institut Teknologi Bandung, Bandung, Indonesia
⁴ Materials Science and Engineering Department, Yeungnam University, Gyeongsan, South Korea

*Corresponding author: andrienurrochman@gmail.com
§ Both authors contributed equally to this work

Abstract. Silver base brazing alloys are commonly used for brazing most of ferrous and nonferrous metals alloys. These families of filler metals have a lower brazing temperature due to Sn addition thus offers excellent flow. Meanwhile, the high content of Ag in the alloys guarantees a good corrosion resistance. However, the detrimental effect was shown when it joints in stainless steel. In present work, corrosion behavior of silver-copper-tin brazing alloy was evaluated. The brazing alloy was exposed to water contained chloride and the temperatures were varied at 25, 40, 55, and 70 °C. The electrochemical methods were utilized to evaluate the corrosion behavior of the alloy. The results showed that the dissolution of Sn seems to be initiating the corrosion of the silver-copper-tin brazing alloy. Nevertheless, the active dissolution of the Cu to the solution simultaneously influence the corrosion behavior of the silver-copper-tin brazing alloy. This study in terms of the alloy corrosion behavior in the particular environment should give both of academicals and industrials contributions.

1. Introduction

Many different types of pure metals and alloys of brazing filler materials are developed. Among them, silver base brazing alloys are commonly used for brazing most ferrous and nonferrous metals and alloys. These families of filler metals have lower brazing temperature and offer excellent flow. Moreover, the silver-copper-tin brazing alloys are free of phosphorus, the element that was believed as the catalyst of the most phosphorus-containing brazing alloy corrosion [1].

Very often failures of the braze joints occurs in the brazing alloys at first [2, 3]. The complex either electrochemical or chemical corrosion process in the brazing alloys builds an aggressive environment that harmful to the base materials. Many brazed joints consist of two or more phases. Sometimes one or more of the phases will be subjected to selective attack. Occasionally, an element is selectively leached from the braze [4]. Thus, corrosion properties of the brazing alloys must be considered when selecting the appropriate brazing alloys. Studies in terms of their behaviour in the particular environment should give both of academicals and industrial contributions.
In the present study, we intended to evaluate the corrosion behaviour of the silver base brazing alloys. This study was focused to the effect of the temperature on corrosion behaviour of silver-copper-tin brazing alloy in chloride containing electrolyte.

2. Experimental Procedures
The materials used were commercial silver-copper-tin brazing alloy and supported by Doosan Heavy Industries & Construction Ltd. The compositions of the brazing alloy are 9.5% Sn, 30.5% Cu, Ag bal. The materials were pre-treated by mechanically polished with SiC abrasion paper from 600 to 2000 grits, and then mirror finished using Buehler polishing cloth wetted with diamond suspension up to 1 µm. Afterwards, the materials were cleaned by ultrasonically degrease for 5 minutes in methanol and ethanol before rinse thoroughly in distilled water before finally dried.

The corrosion behaviour was evaluated by electrochemical method such potentiodynamic polarization, cyclic voltammetry, and potentiostatic polarization. The experiments were conducted using three-electrode cell with the reference electrode used was silver/silver chloride (Ag/AgCl saturated KCl). The condition was under open air atmosphere with varied temperature of 25, 40, 50, and 70°C in 3.5 wt% NaCl electrolyte prepared by using distilled water and analytical grade NaCl.

3. Results and discussions
The potentiodynamic polarization of the silver-copper-tin brazing alloys in 3.5 wt% NaCl solution resulted in E vs log I curves and represented in figure 1. The anodic region at 25°C showed the typical anodic polarization behaviour of Cu-Sn metal alloys in aqueous chloride media [5-8]. The curve consisted of two regions that have minimum current density. The corrosion potential \(E_{corr}\) of the alloy at 25°C in 3.5 wt% NaCl solution was -0.135 V\text{SSCE}\) with the corrosion current of 3.864 \(\times 10^{-7}\) A.

![Figure 1. Potentiodynamic polarization of silver-copper-tin brazing alloy](image1.png)

![Figure 2. Potentiostatic polarization of silver-copper-tin brazing alloy with the potential of 135 mV\text{SSCE} at 25, 40, 55, and 70°C](image2.png)

At higher temperature the \(E_{corr}\) tend to shift towards more noble value with respect to the increased of temperature. The \(E_{corr}\) at 40°C, 55°C, and 70°C are -0.130 V\text{SSCE}, -0.134 V\text{SSCE}, and -0.124 V\text{SSCE}\) respectively. Interestingly, the corrosion current showed the same manner regarding its relationship with the changes of temperature which is tends to increase with the increasing of temperature: 9.72 \(\times 10^{-7}\) A at 40°C, 1.33 \(\times 10^{-6}\) at 55°C, and 1.36 \(\times 10^{-6}\) at 70°C.

It is believed that the material might consists layer of corrosion products that formed during the short preliminary hold time at the free corrosion potential prior the tests [5, 6]. As has been known, temperature favours the kinetics of the reactions, and supposed to have the similar effect with these corrosion products layer forming reactions. Thus, the \(E_{corr}\) was slightly shifted to the noble values with
increasing of temperature. However, since temperature also tends to increase the kinetic of the anodic dissolution reactions, the anodic current densities are higher as temperature increases.

At the $E_{corr}$ corrosion possibly associated with the dissolution of Sn to Sn(II) species [7, 9, 10] based on the following reactions:

\[
\text{Sn} + 2\text{OH}^- = \text{Sn(OH)}_2 + 2\text{e}^-
\]

and/or

\[
\text{Sn} + 2\text{OH}^- = \text{SnO} + \text{H}_2\text{O} + 2\text{e}^-
\]

The passivation of the alloy in the region of the potential slightly above the $E_{corr}$ (denoted as A in figure 1) possibly due to the formation of Sn(IV) species by the following reactions:

\[
\text{SnO} + \text{H}_2\text{O} + 2\text{OH}^- = \text{Sn(OH)}_4 + 2\text{e}^-
\]

The Sn(OH)$_4$ is insoluble and precipitated on the alloy’s surface forming a passivating film. However, chlorination of the corrosive product may occur and the chlorides have incorporated in the lattice of Sn(IV) species. Furthermore, the copper might also form CuCl mixed with the tin rich corrosion product [11, 12]. The Sn(IV) film dehydrates to form SnO$_2$, and resulted decreasing of the current density at the upper region (denoted as B in figure 1) of the potentiodynamic polarization curves particularly at 25°C. These passive films tend to become less stable with increasing of the temperature. At the highest temperature (70°C) the potentiodynamic polarization curve shows that the anodic current density continuously increases.

The potentiostatic experiments were done on purpose to evaluate the passive region as a function of temperature. The curves represented in figure 2 showed that the current resulted from increasing the temperature in the passive region become greater, even so the differences are not large. The current curves showed the highest degree of stability. The potentiostatic curves were also shown no oscillation or abruption, hence it is possible that the alloy was in the passive state with relatively stable passive layer at each of the temperature. Despite the insoluble mixed corrosion product of Sn and Cu, silver as the noblest element in the alloy is seems to have an important contribution to the low current density, either it is in its origin or its oxide form.

Figure 3. Cyclic voltammogram of silver-copper-tin brazing alloy in NaCl 3.5 wt% at 10, 20, 30, 40 mV/s

Figure 4. Silver-copper-tin brazing alloy anodic peak current versus square root of scan rate at 10, 20, 30, 40 mV/s
Voltammograms of the silver-copper-tin brazing alloys in figure 3 showed that the cathodic peak is obviously appeared at any scan rate. Furthermore, the peak increasing in current value along with scan rate. Two peaks of the anodic part are shown and noted as A1, and A2. The A1 peak is well-defined at the small scan rate, then gradually reduced and more like shoulder with increasing scan rate. The dependence of Ea and Ia on the v 1/2 in figure 4 showed a high degree or linearity. The linear relationship between Ia on the v 1/2 described that the anodic reaction was diffusion controlled by the limiting diffusion species. From the report by M. Drogowska et al. [10] the diffusing species differ in nature from the ions already present in solution as OH\(^{-}\), the possibly limited diffusing species is Sn\(^{2+}\). The A1 peak indicated the diffusion-controlled of tin and, subsequently, the formation of porous oxides or hydroxides. Relied on the potentiodynamic polarization curves, good correlation between a small peak near the corrosion potential of the alloy and the first peak (A1) of the alloy’s voltammograms established that the production of chlorinated and porous corrosion product occurred in this region.

The corrosion of the alloy initiated by the dissolution of Sn to the Sn(II) species as proposed by several authors [26-31]. The dissolution of Sn to form Sn(II) species predictically could inhibit the corrosion to progresses. In accordance with the potentiodynamic polarization result, the Sn(OH)\(_2\) and SnO firstly formed and followed by the production of relatively insoluble Sn(OH)\(_4\) and chlorinated corrosion product (possibly SnO\(_x\)(OH)\(_{4-x}\)). nH\(_2\)O, with \(z \leq 1\) and CuCl) before finally resulted the more stable product of SnO\(_2\) that makes the curves decay before reaches relatively steady state at lower current density after slightly increasing at the initial. Since the static polarization experiments have been done at passive region of the alloy (second peak of the minimum current density), the stable passive film of SnO\(_2\) possibly achieved.

4. Conclusion
The dissolution of Sn seems to be initiating the corrosion of the silver-copper-tin brazing alloy. Nevertheless, the active dissolution of the Cu simultaneously influences the corrosion behavior of the silver-copper-tin brazing alloy. A typical anodic dissolution of Cu-Sn metal alloys showed by the alloy. At least two regions of the active-passive transition are observed. These minimum peaks of the current density probably caused by the formation of mixed tin rich insoluble corrosion product and copper corrosion product. The alloy was in the stable passive state regardless the temperature variably.

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