Investigation on Passivation Behavior of Sn-0.7Cu Solder in Different Polarizing Conditions

Wai Kuan Ho¹, Ahmad Azmin Mohamad² and Muhammad Firdaus Mohd Nazeri¹,*

¹School of Materials Engineering, Universiti Malaysia Perlis, 02600 Jejawi, Kangar, Perlis, Malaysia
²School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300, Nibong Tebal, Penang, Malaysia

Abstract. Corrosion behaviour of Sn-0.7Cu solder alloy was evaluated by conducting potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The solder was polarized under the scan rate of 1.0 mV/s and with the scan range from -2 to 1 V SCE. EIS test was performed at the frequency of 10000 Hz to 0.1 Hz. The oxide layer was found on the surface of solder by post-corrosion characterization. XRD results indicate that the main corrosion products formed on the solder after both corrosion tests were tin oxide such as SnO and SnO₂. Porous rod-like structure of corrosion product was observed under morphology analysis of Sn-0.7Cu solder. The corrosion product was represented as tin oxide which matched with the result of XRD.

1 Introduction

Lead solder alloy was heretofore extensively used in electronic devices. The development of lead-free solder was invented lately due to environmental and health concern. The solder alloy was switched to harmless substance for soldering. The tin-silver-copper (SAC) solder alloy is highly recommended due to its advantages in mechanical properties and good solderability and can be used as a lead-free alternative [1]. But, the cost of SAC solder was comparatively high as the presence of silver metal. Sn-Cu solder alloy has become a promising alternative on account of low cost, good solderability and great mechanical properties [2]. This in turn allows Sn-Cu alloy to take the spot as the main candidate to replace Sn-Pb in the applications.

Eutectic Sn-0.7Cu has a comparable melting point (227 ºC) and good fatigue resistance as compared to Sn-Pb solder. This makes Sn-0.7Cu to be used in existing Sn-Pb production lines without much modifications. Corrosion is one of the critical factors for reliable interconnect system. However, it is often overlooked since Sn-Pb alloys are known to produce stable oxide and the galvanic potential difference between Sn and Pb is small [3]. However, for lead-free solder presence of various alloying elements might contribute differently and should be systematically investigated. In this work, corrosion properties of Sn-0.7Cu will be studied in different polarizing conditions of direct current (potentiodynamic

* Corresponding author: firdausnazeri@unimap.edu.my
polarization) and alternate current (electrochemical impedance spectroscopy, EIS). Further supporting characterizations on microstructure and phase changes will also be reported.

2 Methodology

Pellets of Sn-0.7Cu solder were prepared in 3 mm and 5 mm, thickness and diameter, respectively. Each solder pellets were attached to Cu wire and cold-mounted for ease of handling during grinding and polishing. The samples were ground with SIC paper from grit 400 to 1200 and polished with the aid of 1 micron of alumina solution in order to obtain mirror surface finish. Initial characterization was performed under scanning electron microscopy (SEM) with model of JEOL 6460-LA and Shimadzu X-ray diffraction 6000 diffractometer (XRD). SEM was used for morphological analysis. XRD analysis performed at 20 values which are ranging from 20° to 90° with a medium scan rate at 5 °C per minute. Cu-Kα radiation was used to investigate the phases exist in the solder pellet and the result was matched with the standard phase identification from International Committee of Diffraction Data (ICDD) X-ray data. For the corrosion analysis, three electrodes compartment cell was prepared. Sn-0.7Cu solder was acted as working electrode while platinum rod and saturated calomel electrode (SCE) were counter and reference electrode respectively. Potentiodynamic polarization test was carried out by immersed the three electrodes into a 1 M hydrochloric acid (HCl) and polarized at the scan rate of 1.0 mV/s and scan ranges in between -2 V_SCE to 1 V_SCE. Electrochemical impedance spectroscopy (EIS) was performed under the frequency of 10000 to 0.1 Hz and with 10 mV amplitude of AC. The tests were measured by using potentiostat with the model of AUTOLAB PGSTAT 30.

3 Results and Discussion

3.1 Initial Phase Characterization

XRD analysis of Sn-0.7Cu solder before corrosion test revealed the presence of two phases which are the β-Sn (ICDD 01-075-9188) and monoclinic Cu₆Sn₅ (ICDD 01-076-2704) intermetallic compounds (IMC), as shown in Figure 1. The phases obtained was similar in accordance with the previous research where β-Sn matrix was the Sn-rich phase. The phase of Cu₆Sn₅ was produced due to the limited solubility of Cu in Sn. During reflow process, the Cu reacted with the Sn to form Cu₆Sn₅ intermetallic compounds and distributed in the β-Sn matrix [4].
3.2 Corrosion analyses

The potentiodynamic polarization plot for Sn-0.7Cu consisted of two main regions which were anodic and cathodic regions (Fig. 2). In cathodic region, the applied potential increased gradually starting from -2 \text{V}_{\text{SCE}}. This resulted in the reduction of the current density from point A to B, normally associated with reaction [4]:

\[
O_2 + 4e^- + 4H^+ \rightarrow 2H_2O
\]  

(1)

A slightly fluctuation in the curve at cathodic region was basically due to evolve of hydrogen bubble gas. Beyond point B, anodic reaction started with the increasing of current density with potential. This region was considered as the primary active region of the polarization process. Dissolution of active metal occurred at this region. Sn was highly reactive than Cu due to the electrode potential in electrochemical series. Thus, Sn metal will be dissolved by oxygen into metal ions [4]:

\[
Sn \rightarrow Sn^{2+} + 2e^-
\]  

(2)
The linear region between the point B and C considered as anodic slope while the linear region between point A and B was the cathodic slope. The corrosion potential (E$_{corr}$) and corrosion current density (I$_{corr}$) can be obtained from the interception point of both slope as plotted on the polarization curve. The E$_{corr}$ and I$_{corr}$ were -521 mV and 0.00017 A/cm$^2$, respectively. The primary activation region was ended at point C where the current density reached the maximum value. The region beyond point C to point D is known as the passive region. At point C, the passivation potential was the indicator to separate the active and passive region. Passivation current density (I$_{pass}$) was exploited to describe the passivation behaviour of the solder. The passive region was continued to point D and the current density remained unchanged. The development of the passive region was due to the reaction of Sn$^{2+}$ ions with the hydroxide ions (OH$^-$) to form oxide on the surface of solder through the reaction [4]:

\[
2\text{Sn}^{2+} + 2\text{OH}^- \rightarrow 2\text{SnO} + 2\text{H}^+ \quad (3)
\]

\[
\text{Sn} + 2\text{H}^+ \rightarrow \text{Sn}^{2+} + \text{H}_2 \quad (4)
\]

\[
2\text{Sn}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{Sn(OH)}_4 + 4\text{H}^+ \quad (5)
\]

\[
\text{Sn(OH)}_4 \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} \quad (6)
\]

Nyquist plot for EIS measurement consisted of the semi-arc that depicted the corrosion performance of solder (Figure 3). The small semi-arc illustrated the start of dissolution of Sn metal to Sn metal ions. The formation of oxide passive layer was indicated by drop of Z$'$ (imaginary axis). The layer was indicated as the obstacle to prevent the corrosive ions from attacking the Sn-0.7Cu solder. Warburg impedance was existed as diffusion process once the passive oxide layer breakdown. The Warburg impedance was presented as a steep line which connected to the semi-arc and disclosed the corrosion kinetic of the Sn-0.7Cu solder. EIS measurement was determined by the fitting of experimental data with an equivalent circuit. The fitting quality was evaluated by chi-squared ($\chi^2$) values. The interpretation of physical elements of the proposed electrical equivalent circuit as showed in Figure 3a. In the first layer, Rs was the resistance of 1 M HCl solution and R1 and R2 in second and third layer were the resistance of porous and barrier layer respectively. Besides, the CPE1 and CPE2 were related to the capacitance of the porous layer and barrier layer correspondingly. At the second layer of the circuit, R1CPE1 represented the occurrence of metallic corrosion where the charge transfer occurred while R2CPE2 represented the diffusion process.
Fig. 3. (a) Equivalent circuit and (b) Nyquist plot for Sn-0.7Cu in HCl.

In this circuit fitting, the chi-squared value was $9.28 \times 10^{-4}$. Based on the previous research, good fitting of the Nyquist plot was in the range of $10^{-4}$ to $10^{-3}$. The summary of the values of electrical equivalent circuit were summarized in Table 1. $R_2$ value was indicated that the oxide layer was formed and acted as a barrier to block the corrosion process while $CPE_2$ value was specified the compactness of the oxide layer formed.

### Table 1. Resistance value of electrical equivalent circuit

| Element       | Value           |
|---------------|-----------------|
| $R_s$ (Ω cm²) | 3.14            |
| $CPE_1$       | 0.0764          |
| ($\Omega^{-1}$ cm² sⁿ) |            |
| $R_1$ (Ω cm²) | 0.0589          |
| $CPE_2$       | 1.5344          |
| ($\Omega^{-1}$ cm² sⁿ) |            |
| $R_2$ (Ω cm²) | 0.8705          |
| $\chi^2$      | $9.28 \times 10^{-4}$ |

### 3.3 Post-corrosion characterizations

The micrographs of Sn-0.7Cu solder polarized in 1 M HCl solution can be clearly observed under SEM as shown in Figure 4. The corrosion products with rod-like structure were loosely distributed on the surface of the solder with different orientations and was not fully covering the surface of the solder in both potentiodynamic polarization (Fig. 4a-b) and EIS (Fig. 4c-d). Tin oxide was found in the corrosion products which transformed from the reaction between Sn and corrosive solution. The existence of the halide ions (Cl⁻) in corrosive solution, which was destructive to the intact surface of the solder [5]. As a result the passivation film produced were porous and offer relatively weak protection towards the solder in the long term exposure to HCl.
Fig. 4. SEM micrographs of Sn-0.7Cu solder after potentiodynamic polarization at magnification of (a) x1000, (b) x5000, after EIS (c) x1000, (d) x5000.

Phase analysis of Sn-0.7Cu solder after potentiodynamic polarization (Figure 5a) and EIS (Figure 5b) showed four different phases that existed. The corrosion products of SnO (ICDD 01-077-2296) and SnO₂ (ICDD: 01-071-5330) were identified along with the original phase of β-Sn (ICDD 01-075-9188) and monoclinic Cu₆Sn₅ (ICDD 01-076-2704). Presence of comparable phases in both polarizing conditions was due to the similarity of the experiment conditions without altering any parameters.
4 Conclusion

The electrochemical corrosion behavior of Sn-0.7Cu has been investigated through potentiodynamic polarization and EIS analysis. In potentiodynamic polarization testing, this solder was shown to produce passivation abilities in 1 M HCl solution. This is further supported by the finding in EIS. XRD analysis confirmed the existence of passive oxide film which formed by corrosion by-product of SnO and SnO$_2$ that act as a protection film to increase the corrosion resistance. However, the nature of the film was found to be porous in both polarizing conditions revealing insufficient protection for prolonged period in this acidic condition.

The authors would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of FRGS/1/2019/TK05/UNIMAP/02/5 from the Ministry of Education Malaysia.

References

1. Wang, M., J. Wang, and W. Ke, Mic. Relib. 73, (2017)
2. Li, G., Y. Shi, H. Hao, Z. Xia, Y. Lei, and F. Guo, J. Alloy. Compd. 491, (2010)
3. Song, F. and S.R. Lee. 56th Electronic Components and Technology Conference. IEEE, (2006)
4. Rasid, M., Z. Azwan, M.H. Zainol, M.F. Omar, M.N. Derman, M. Nazeri, and M. Firdaus. Solid State Phenomena, (2018)
5. Li, D., P.P. Conway, and C. Liu, Corros. Sci., 50, (2008)