Corrosion Assessment of Sn-0.7Cu Lead-Free Solder in 1 M Hydrochloric Acid

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Abstract. The corrosion performance of Sn-0.7Cu solder alloy is investigated in 1 M Hydrochloric acid by means of potentiodynamic polarization technique at the scan range of -2V SCE to 1 V SCE was applied to the sample at the scan rate of 1mV/s. Supporting morphological analysis was done by using Scanning Electron Microscope while phase analysis was confirmed by using X-ray Diffraction analysis. Morphological analysis showed two type of oxide layer has formed as corrosion product, which are compact oxide layer and loose rod-like oxide layer after corrosion analysis which confirmed to be SnO and SnO₂. This indicate that complete protection from further corrosion was impossible due to the incomplete passivation layer formation.

1 Introduction

Soldering is one of the metallurgical joining technique that use solder as filler metal for joining two metal. Formation of intermetallic compound is a chemical reaction that bond the solder and metal substrate. It is widely used in electronic industry as by definition, soldering needs relatively low temperature for processing as it contain element with lower melting points [1, 2]. Traditional solder or known as eutectic lead solder have been used for joining alloys at low temperature especially in electronic industry which serve as interconnects that able to provide the conductive path to connect from one circuit to another due to their good combination of material properties, process attributes and low cost.

Restriction of Hazardous Substances (RoHS) originated in the European Union and the usage of dangerous material in electric and electronic product. Lead is one of the 10 hazardous materials that restricted by RoHS and this apply to all European Union has ban from using in electronic products by 1 July 2006[3]. Sn-0.7Cu eutectic alloy is toxic free solder alloy with no lead contained alternative having a melting temperature 227°C. However, alternative solder alloys must need to complete various requirements like chemical or physical properties and cost which mean that the melting temperature, strength and integrity and others should also be similar or better than Sn-Pb alloy, and manufacturing costs must be competitive [4]. The distribution of Cu in Sn-0.7Cu solders is crucial to understand

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the morphology of this binary solder. Two typical regions can be observed in Sn-0.7Cu alloy which are Cu6Sn5 and the Zn-rich phase. The bright grey regions show β-Sn matrix and is primarily solidified, whereas in dark region represents intermetallic compound (IMC). This show the IMC is one of the important factor to enhance the mechanical properties of Sn-0.7Cu solder alloy [5].

A number of literature studies focused on correlations between the microstructure and the properties associated with a number of solder alloys. However, there is a lack of studies of electrochemical corrosion behaviour of Sn–0.7Cu solder alloy when exposed to an acid medium. A solder alloy requires good corrosion behaviour, especially when the solder joints are directly exposed to aggressive medium in an industrial environment [6-8]. Most of the studies developed the corrosion behavior of Sn–Cu alloys in NaCl and KOH solution [7, 9, 10]. In this work, corrosion performance of Sn–0.7Cu solder alloy will be investigated in 1 M HCl by using potentiodynamic polarization. Subsequent characterization techniques of XRD and SEM will be implemented to support the electrochemical findings.

2 Methodology

The Sn-0.7Cu solder was produced into 5 mm diameter and 3 mm thickness pellets. Copper wire was attached on the solder alloy using soldering process. The solder was then mounted with epoxy resin which mixed with epoxy hardener with ratio of 1:1. Mounted samples had undergone grinding and polishing using surface grinder machine to produce a smooth and mirror-like surface.

A potentiostat (Autolab PGSTAT 30) was used for electrochemical corrosion analysis of Sn-0.7Cu in 1 M HCl. For potentiodynamic polarization, scan potential range of -2 V SCE to 1 V SCE was applied on sample at the scan rate of 1mV/s. Saturated Calomel Electrode (SCE) used as reference electrode while platinum work as counter electrode in potentiodynamic polarization analysis analysis.

For characterization, X-ray Diffraction (XRD) model (Shimadzu XRD 6000) was used for phase analysis of Sn-0.7Cu before and after corrosion analysis. The analysis is performed from 20°-90° with the scan rate of 5°/min used. The profile pattern was identified using Xpert Highscore Plus software. Scanning Electron Microscope (SEM), JEOL JSM-6460-LA was used for morphological analysis of sample before and after electrochemical testing.

3 Results and Discussion

3.1 Corrosion Analysis

Potentiodynamic polarization testing of Sn-0.7Cu was carried out in 1M HCl. The cathodic current starts from point A at a potential value of -2.00 V SCE and ended at point B with potential value of -0.53V SCE with the current density decreased sharply from 269 μA to approximately 0.60 μA. The slope intersection of linear region between cathodic region and anodic region represent corresponding corrosion current (Icorr) and corrosion potential (Ecorr) of Sn-0.7Cu solder alloy.

Beyond point C, the current was slightly decrease which representing the initiation of passivation for Sn-0.7Cu at this particular region or in other word is known as passive region. Sn²⁺ ions had deposit on the surface of Sn-0.7Cu solder alloy and forming a passive film. As the applied potential increase, the current density continue reduce until the formation of full oxide film on the surface of the Sn-0.7Cu.

Path CD shows the passive region in polarization study on Sn-0.7Cu. Passive current density (iP) with approximate value of 0.0063A, is the minimum current required for
maintaining the oxide film along passive region [11, 12]. The current is maintained and independent with the increasing of applied potential. This shows that the surface of Sn-0.7Cu solder alloy is covered with passive film. The Sn-0.7Cu solder alloy was remained stable and passive state until the end of the polarization.

Fig. 1. Potentiodynamic polarization graph of Sn-0.7Cu.

3.2 Phase analysis

X-ray diffraction (XRD) analysis was conducted on Sn-0.7Cu solder alloy before (Figure 2a) and after polarization (Figure 2b). The as-prepared Sn-0.7Cu consist of only two phases, which is body centered tetragonal $\beta$-Sn (ICDD: 00-004-0673) and monoclinic Cu$_6$Sn$_5$ (ICDD: 03-065-2303). Meanwhile for the XRD analysis after potentiodynamic polarization, two new phases were observed, SnO (ICDD: 00-050-1429) and SnO$_2$ (ICDD: 00-006-0395). This has proved that the dissolution of Sn is occurred and further react with OH$^-$ to form SnO and SnO$_2$. The obtained result is same with the report of Huang et al. [13] which SnO and SnO$_2$ were the passivation barrier for the Sn-0.7Cu solder alloy to prevent further corrosion. The equations involved:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (1)$$
$$Sn \rightarrow Sn^{2+} + 2e^- \quad (2)$$
$$2Sn^{2+} + 2OH^- \rightarrow 2SnO + 2H^+ \quad (3)$$
$$Sn + 2H^+ \rightarrow Sn^{2+} + H_2 \quad (4)$$
$$2Sn^{2+} + O_2 + 6H_2O \rightarrow 2Sn(OH)_4 + 4H^+ \quad (5)$$
\[ 2\text{Sn(OH)}_4 \rightarrow 2\text{SnO}_2 + 4\text{H}_2\text{O} \]  \hspace{1cm} (6)

### 3.3 Morphological Analysis

The corrosion product found on Sn-0.7Cu after potentiodynamic polarization (Figure 3). After electrochemical analysis, the surface of the sample looks roughen and expected contributed by to be the formation of SnO and SnO\(_2\). This passivation layer act as an important barrier against the corrosion. In general, the corrosion product is made of arrangement of rod-like corrosion product hence producing two differently distributed passivations layers of compact oxide layer and loose oxide layer. Loose oxide layer was the oxide layer that do not passivate completely. Loose oxide reveals that the corrosion is still incomplete and further oxidation may occur at the certain part [14].

![Fig. 2. XRD pattern of Sn-0.7Cu (a) before corrosion and (b) after potentiodynamic polarization.](image)
4 Conclusion

The electrochemical corrosion behavior of Sn-0.7Cu has been investigated through potentiodynamic polarization analysis. In potentiodynamic polarization testing, this solder was shown to produce passivation abilities in 1 M HCl solution. XRD analysis confirmed the existence of passive oxide film which formed by corrosion by-product of SnO and SnO₂ that act as a barrier to increase the corrosion resistance. However, morphological analysis had found some that the passivation layer contained porous region made of loose-oxide formation. This was identified as weak spot for full corrosion protection.

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