Corrosion Properties of SAC305 Solder in Different Solution of HCl and NaCl

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Abstract. Potentiodynamic polarization was used to studied the corrosion properties of SAC305 solder in different solution of 1.0 M HCl and 3.5 wt.% NaCl using the same scanning rate of 1.0 mV/s. The polarization curves indicated that corrosion in NaCl was less severe than in HCl solution based on corrosion current and passivation behavior obtained. Morphology and phases obtained after corrosion using SEM and XRD were analyzed. Microstructure analysis shows the present of compact corrosion product with presence of larger flake for polarization in NaCl compared to HCl. Phases present in XRD analysis confirmed the present of SnO and SnO₂ corrosion product for sample from both solutions.

1. Introduction
Traditional Sn-Pb solder has been used as joining materials in many industries especially in electronic industries. However, international legislation on lead (Pb) due to high toxicity has leads to the industrial needs to find other new solder as its replacements [1-5]. The research and development were then conducted intensively to search for lead-free solder. Currently, applications of lead-free solders such as tin-silver (Sn-Ag) [6-8], tin-zinc (Sn-Zn) [4, 9], tin-copper (Sn-Cu) [10, 11] and tin-silver-copper Sn-Ag-Cu (SAC) [2, 6, 12-16] have been developed in electronic products. Among them, eutectic SAC305 is one of the most promising candidates to replace the traditional Sn-Pb solder alloys. Properties of SAC305 such as good thermal, mechanical, fatigue properties and low melting temperature make it as one of the most favorable lead-free solder candidates.

Reliability of solder is very crucial in determining performance and endurance of electronics devices during application [10, 17]. Among properties related to reliability includes coefficient of thermal expansion, intermetallic compound formation, fatigue strength, mechanical strength and corrosion [8, 11, 16]. For the solder to be considered as direct replacement for Sn-Pb, it must have oxidation or corrosion resistance in various conditions such as salt-water, moist or air contaminations environments [2, 3, 11, 18]. Since the uses of electrical devices are everywhere, the understanding of the effect of corrosive media to the corrosion of lead-free solder is needed.
Rosalbino et al. [13] has reported the addition of copper (Cu) has improve the corrosion resistance of Sn-Ag solders alloy, where the passivity behavior of alloys was enhanced compared to traditional Sn-Pb solder alloy. Meanwhile, Wislei et.al [11] revealed that the distribution of fine and homogenous Ag$_5$Sn intermetallic particles in Sn-rich matrix plays major role in corrosion resistance, as galvanic coupling in between phases may dictate corrosion performance of SAC305. So far, most of corrosion performance studies of SAC305 are limited to NaCl [12] and KOH [19] solutions, where the corrosion of SAC305 solder in common acidic corrosive media such as hydrochloric acid (HCl) still remain limited. Thus, current study focused on the effect of 1 M HCl solution on the corrosion performance of SAC305. The corrosion characteristics will be compared with 3.5 wt % NaCl. Morphological, elemental and phases analyses were also discussed to support the findings.

2. Experimental

The solder wire of commercially supplied SAC305 (Dagu Electronic) was placed in clean crucible after rolled into coils. The crucible was then placed in a muffle furnace set with highest temperature of 300°C. The melted SAC305 solder then left to cool at room temperature. Hydraulic Press 20 Ton (10 Mpa) used to pressed solidified alloy to obtain constant thickness of 3 mm. Puncher was used to punch the solder into solder pellet with diameter of 5 mm and thickness of 3 mm. Copper wire with length of 3 cm was then solder with solder pellet to provide current flow. Wire-attached solder pellets were cold mounted with epoxy resin and then were ground and polished to mirror finish prior corrosion testing.

Acid solutions of HCl with concentration of 1.0 M and NaCl solution with concentration of 3.5 wt. % were prepared for the potentiodynamic polarization analysis. Standard three electrode system consists of platinum as counter electrode, Saturated Calomel Electrode (SCE) as reference electrode, and SAC305 solder as working electrode were used to carry out potentiodynamic measurements. Potentiostat (Autolab PGSTAT 30) was used to undergo potentiodynamic polarization test. Scanning rate was set to 1.0 mV/s, with applied potential range of -2.0 to 2.0 V$_{SCE}$ for both solutions. The electrochemical characterization was carried out three times to ensure reproducibility of the results.

Scanning electron microscope (NOVA NANOSEM 450) equipped by energy dispersive spectroscopy (X-Max 50, OXFORD) was used to determine the microstructure and corrosion products compositions of SAC305 solder after corrosion testing. Phase analysis was run by X-Ray Diffractometer (Shimadzu XRD 6000) at 2θ ranging from 20 to 90°. XPERT Highscore Plus software was then used to analyze the results obtained in accordance to International Committee of Diffraction Data (ICDD) X-Ray data files.

3. Results and Discussions

3.1 Potentiodynamic Polarization Analysis

Potentiodynamic polarization curve for SAC305 in 1.0 M HCl can be divided into two different regions namely cathodic and anodic regions (Figure 1). The scan starts at potential of -2.0 V in the cathodic region. In general, the cathodic region involved the process of oxygen and reduction [5]. As the potential increases, the current decrease rapidly. The point intersection between cathodic and anodic slopes represents the equilibrium corrosion potential ($E_{corr}$) and equilibrium corrosion current density ($i_{corr}$). Further increase in applied potential resulted in rapid increase of current density up to point “A” signifies anodic region where dissolution of Sn actively occurs.
As the potential continues to increase slightly, the current decreases reaching point B. The corresponding potential and current density are known as primary passive potential ($E_{pp}$) and critical current density ($i_{crit}$). At this point, the solder reaches the highest corrosion rate and the current density changes from active to passive state, where the oxide film of tin oxide starts to form at the solder surface due to reaction between Sn and O in the aerated solution that leads to the reduction of current density up to lowest passivation current value ($i_p$). Beyond $i_p$, a sharp increase in current density is observed normally caused by the breakdown of oxide film. On further scanning to region C, the opposition between the formation of oxide film and dissolution of Sn results in the current remains independent to applied potential, indicates the onset of pseudopassivation process.

Figure 1. Potentiodynamic polarization curve of SAC305 solder in 1.0 M HCl

Comparing the polarization curves in between 1.0 M and 3.5 wt.% NaCl, almost similar behavior in the cathodic region was seen (Fig. 2). On the other hand, the differences start in the anodic region. For polarization in HCl solution, the value of $E_{corr}$ obtained was -0.7133 mV which is higher than polarization in NaCl (-1.052 V SCE). Meanwhile, the corrosion current density in HCl is 39.83 µA which higher than polarization in NaCl at value of 2.19 µA revealing that the kinetics of reaction in HCl is higher than in NaCl. The passivation in NaCl happen in three stages while in HCl only happen in two stages. This indicates that passivation in NaCl is better than in HCl. In addition, the value of $i_p$ for polarization in NaCl at 0.0105 µA is lower than in HCl solution (0.0506 µA). This shows that less current corresponds to the thickening the oxide film at solder surface is required.
**Figure 2.** Potentiodynamic polarization curve of SAC305 solder in 1.0 M HCl and 3.5 wt.% NaCl solution at 1.0 mV/s scanning rate

**Table 1.** Corrosion parameters obtain from polarization graph

| Solution            | $E_{\text{corr}}$ (V) | $i_{\text{corr}}$ (µA) | $i_p$ (A) |
|---------------------|------------------------|-------------------------|-----------|
| 1.0 M HCl           | -0.7133                | 39.83                   | 0.0506    |
| 3.5 wt.% NaCl       | -1.052                 | 2.19                    | 0.0105    |

**3.2 Morphology analysis**

Figure 3(a) shows the microstructure of as-prepared SAC305 solder. The results show the presence of typical three-phase appearance which were $\beta$-Sn matrix, Ag$_3$Sn (grey crystal) and Cu$_6$Sn$_5$ (black crystal). The results on the microstructure of SAC305 solder in HCl and NaCl solution shows in Figure 3(b) and 3(c). SAC305 polarized in HCl solution shows the formation of more loosely-packed oxide film with the present of pitting. Meanwhile, the microstructure of SAC305 solder polarized in NaCl solution shows more compact corrosion product (Figure 3(b)), of which is comparable with the results reported Rosalbino et.al [12] and Dezhi et.al. [14]. Presence of obvious pitting highlights that the corrosion attack in HCl is more severe that allows little recovery in the damaged passivation film.

Data obtained from the EDX analysis (Table 2) shows the addition presence of O at the surface which present by the formation of SnO and SnO$_2$ oxide film for solder in both solutions. Based on the data, the loss of Sn in HCl solution was higher compared in NaCl solution indicating that the dissolution of Sn is worse in HCl solution.

**Table 2.** Data on EDX analysis on SAC305 solder for before polarize and after polarize in HCl and NaCl solution

| Sample SAC305 solder | Sn (wt.%) | Ag$_3$Sn (wt.%) | Cu$_6$Sn$_5$ (wt.%) | O (wt.%) |
|----------------------|-----------|-----------------|---------------------|---------|
| As-prepared          | 92.67     | 3.80            | 3.54                | -       |
| Polarization in 1.0 M HCl | 27.21 | 49.17           | 14.30               | 9.32    |
| Polarization in 3.5 wt.% NaCl | 69.88 | 20.07           | 0.34                | 0.61    |
Fig. 3. Microstructure of (a) as prepared SAC305 solder, after potentiodynamic polarization in (b) 1.0 M HCl and (c) 3.5 wt.% NaCl

3.3 Phases analysis of SAC305 solder before and after polarization

Phases analysis was conducted on the sample of SAC305 solder for before and after polarization presented in Figure 4. For as-prepared sample, the XRD results shows the presence of three main phases which are $\beta$-Sn, $\text{Ag}_3\text{Sn}$ and $\text{Cu}_6\text{Sn}_5$ attributed by the limited solubility of Ag and Cu in Sn as the main element, similar to the solubility of Cu in $\varepsilon$ phase and Ag in $\eta$ phase. This statement also in agreement with [12].

The XRD results for after polarize shows that SAC305 solder has the same corrosion product, which was SnO and SnO$_2$ in both solutions. As the most electrochemically active element in this solder system compared with $\text{Ag}_3\text{Sn}$ and $\text{Cu}_6\text{Sn}_5$, Sn is first to dissolved. Therefore, the oxide film forms is Sn-based corrosion product. Furthermore, SEM and EDX analyses show confirmation of the presence of SnO and SnO$_2$ corrosion product at the surface which was consistent with XRD analysis. Cathodic region are generally correlated to the reduction of dissolved oxygen $\text{O}_2$ into $\text{H}_2\text{O}$ [3, 5, 14]:

$$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad (1)$$

The anodic current begins at the turning point of the graph where in SAC305 solder, Sn was the most reactive material therefore Sn tends to dissolved [14]:

$$\text{Sn} \rightarrow \text{Sn}^{2+} + 2e^- \quad (2)$$
Figure 4. XRD of (a) as-prepared SAC305 solder and polarization of SAC305 in different solution (b) 1.0 M HCl and (c) 3.5 wt.% NaCl

As the solder polarize further, SnO forms from the dissolved Sn$^{2+}$ ions to Sn(OH)$_2$. mH$_2$O, and Sn$^{2+}$ ions are simultaneously oxidized gradually by oxygen to form SnO$_2$. This equation was also reported in other research [14, 20]:

$$Sn + 2H^+ \rightarrow Sn^{2+} + H_2$$ (3)

$$2Sn^{2+} + O_2 + 6H_2O \rightarrow 2Sn(OH)_4 + 4H^+$$ (4)

$$Sn(OH)_4 \rightarrow SnO_2 + H_2O$$ (5)

$$Sn^{2+} + 2H_2O \rightarrow Sn(OH)_2 + 2H^+$$ (6)

$$Sn(OH)_2 \rightarrow SnO + H_2O$$ (7)

Based on previous research of Rosalbino et.al [12] [13] and Dezhi et.al [14], the corrosion product at SAC solder surface were tin oxychloride or oxyhydrochloride. However, in present research, corrosion product of SnO and SnO$_2$ were the only corrosion product found at the solder surface. According to Mohanty [15] the other corrosion product forms was SnCl phase, but due to the machine or experimental error, SnCl phase is not detected.

4. Conclusions
As the conclusion, polarization in acidic solution (HCl) resulted in worse corrosion attack based on the higher value of $i_{corr}$. The passivation behavior of SAC305 in HCl was inferior compared in NaCl solution. The oxide film formed was SnO and SnO$_2$ which was the same for both HCl and NaCl solution although the solution is different.

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6. References
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