Corrosion Behaviour of Sn-based Lead-Free Solders in Acidic Solution

Nordarina J¹, Mohd H Z¹*, Ahmad A M² and Muhammad F M N¹

¹Centre of Excellent Geopolymer & Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis, 02600 Jejawi, Arau, Perlis, Malaysia
²School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

E-mail: hafizzainol@unimap.edu.my

Abstract. The corrosion properties of Sn-9(5Al-Zn), Sn-Cu and SAC305 were studied via potentiodynamic polarization method in an acidic solution of 1 M hydrochloric acid (HCl). Sn-9(5Al-Zn) produced different polarization profile compared with Sn-Cu and SAC305. The morphological analysis showed that small, deep grooves shaped of corrosion product formed on top of Sn-9(5Al-Zn) solder while two distinctive structures of closely packed and loosely packed corrosion product formed on top of Sn-Cu and SAC305 solder alloys. Phase analysis revealed the formations of various corrosion products such as SnO and SnO₂ mainly dominant on surface of solder alloys after potentiodynamic polarization in 1 M hydrochloric acid (HCl).

1. Introduction
Rapid growth of science and technology has forced many researchers to ramp up scientific researches and investigations especially in electronic field. Not to be left behind, soldering technology are indeed need to catch up this rapid growth of the current situation of technology. From the usage of lead solder (Sn-Pb), the soldering technology has step into new paradigm towards greener soldering technology. This is mainly cause by law that has restricted the used of lead (Pb) due to high toxic content. It has been banned by the European Union back in February 2003 [1,2].

Joining the team to upgrade the solder performance, many efforts has been gathered all around the world to specify new recipe for new solder technology to change the usage of Pb in solder. Obviously addition and blending of new materials could specifically give solution to different problems. Example are addition of indium (In), copper (Cu), zinc (Zn), argentum (Ag) and gold (Au) [3,4]. However, addition of Zn and Cu has attract great interest towards research especially due to availability of both elements as well as promising future due to excellent properties of both Zn and Cu [5].

Sn-Ag-Cu (SAC) and Sn-Cu alloys are popular by researchers due to low melting temperatures and have excellent wettability as compared to Sn-Ag alone. Due to its popularity gained, SAC305 has been widely applied in microelectronic industry commercially [6]. Meanwhile, Sn-Zn captured the researchers as it also has low melting temperature that are close to Sn-Pb, good mechanical properties and low in cost [7,8]. In addition, addition of Al in Sn-Zn to produce Sn-9(5Al-Zn) solder has shown to passivation on the surface of solder [9]. However, there are limited research focuses on the
corrosion behaviour especially in acidic solution. With most of recent studies limited to NaCl solution, it is worth to investigate other common corrosive solutions such as hydrochloric acid (HCl) to provide better understanding of lead-free solders.

Expanding demand for reduced size and compact electronic products has intrigued the degradation of solder materials. It embarks serious issues in term of product reliability and suggested that system failure could occur due to corrosion [10]. In this work, the corrosion performance of Sn-9(5Al-Zn), Sn-Cu and SAC305 in 1 M HCl will be studied.

2. Materials and Method

2.1 Sn-9(5Al-Zn) solders alloys preparation
The master alloy of 5Al-Zn was prepared by melting pure Al and Zn (Sigma-Aldrich). Mixture of 91% Sn and 9% 5Al-Zn were weighed and re-melted in a porcelain crucible using an induction furnace at 550 °C with the presence of nitrogen gas. The molten alloys were stirred to homogenize the chemical composition. The produced ternary Sn-9(5Al-Zn) solder was cast and air-cooled to room temperature. After cooling to room temperature, the alloy was pressed and mechanically punched to produce pellets with diameter of 5 mm and 3 mm thickness. Each solder pellet was attached to a copper (Cu) wire with 1 mm diameter to provide electrical connections. The alloys were cold-mounted with epoxy resin and were ground, polished and cleaned to obtain a mirror finish surface prior to electrochemical analysis.

2.2 Sn-Cu and SAC305 solders alloys preparation
Sn-Cu and SAC305 (Dagu Electronic) wire that are commercially available was re-melted in muffle furnace at 300°C. Then, the solder was cooled to room temperature and mechanically pressed by using hydraulic press to acquire constant thickness of 3mm. The solder plate was punched to pellet size with diameter of 5 mm each and was soldered to copper wire to provide electrical connection. Samples were later cold mounted and proceed to grind, polish and clean to mirror finish before corrosion analysis.

2.3 Electrochemical analysis
Potentiodynamic polarization were performed using three-electrode system consist of a platinum plate as counter electrode, a saturated calomel electrode (SCE) as reference electrode and the solder material as the working electrode. Potentiostat (AUTOLAB PGSTAT 30) was used to conduct the corrosion test of Sn-9(5Al-Zn), Sn-0.7Cu and SAC305 in 1 M HCl electrolyte. The scan potential range are set from -2.0 up to 2.0 V_SCE with the scan rate used at 1mVs.

2.4 Morphology and structural analyses
The microstructural characterization and corrosion products composition were analysed using field emission scanning electron microscope (NOVA NANOSEM 450). The phase characterization was conducted by X-Ray diffractometer (Shimadzu XRD 6000) at 20 values ranging from 20 to 90 °. The XRD results were analysed by using X’pert HighScore Plus software to match the corresponding peaks with the standards from International Committee of Diffraction Data (ICDD) X-ray data file.

3. Results and Discussion

3.1 Electrochemical analyses
Polarization profiles for Sn-9(5Al-Zn) solder alloys were differed from Sn-Cu based solder. Sn-9(5Al-Zn) solder alloys showed distinctive active-passive behaviour with two stages of passivation occurred. Meanwhile, Sn-Cu and SAC305 only consists of one passivation stage (Figure 1). Cathodic region of Sn-9(5Al-Zn), Sn-0.7Cu and SAC305 started at potential -2.0 V_SCE. From point A , the cathodic scan for Sn-9(5Al-Zn) ended at potential value -0.95 V_SCE. For Sn-Cu and SAC305, the potential ended at value of -0.64 and -0.67 V_SCE at point C. Region AB and AC mainly refers to reduction of dissolved oxygen O_2 into H_2O in aerated HCl electrolyte.
\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \]  

Starting from point B and C, current rapidly increased as potential increased. This is refers to active region. Here are the critical stages in polarization where the dissolution of metal occurs. For Sn-9(5Al-Zn), the current increased sharply from $2.5 \times 10^{-4}$ A. This value is larger as compared to $0.9 \times 10^{-4}$ for Sn-0.7Cu and $1.7 \times 10^{-4}$ for SAC305. In Sn-9(5Zn-Al) system, Zn is the most active material while for Sn-Cu and SAC305 solder alloys, Sn is the most active material [11]. This occurrence made Zn and Sn the first element to be removed during polarization. Since Zn is more reactive as compared to Sn, it is easier to dissolve from Sn-9(5Al-Zn) solder. Besides that, the galvanic corrosion effect is more severe due the presence of Zn/Sn and Zn/Al couplings in the system. However, in Sn-Cu based solder system, even though Sn is the most reactive material, it still has higher value of potential in electrochemical series, plus with abundant amount of Sn which helps to withstand degradation of the metal itself.

The first stage of passivation for Sn-9(5Al-Zn) took place at point D before re-activate and end up with passivation of second stage. This finding is similar with Nazeri et. al [11] where after primary dissolution occurred, a short passivation will undergo before re-activation and re-passivation occurred again. However, this phenomena cannot be found in Sn-Cu or SAC305 system. All three solders started to passivate at point E onwards. At the end of this passive region, the current has become almost independent with applied potential. Usually, the end product from This regions are reported as metal oxide such as SnO and ZnO [12].

![Figure 1. Potentiodynamic polarization of SAC305, Sn-Cu and Sn-(5Al-Zn) in 1 M HCl electrolyte.](image)

| Solder                | $E_{\text{corr}}$ (V SCE) | $I_{\text{corr}}$ (A) | $I_{\text{pass}}$ (A) |
|-----------------------|--------------------------|------------------------|------------------------|
| Sn-9(5Al-Zn)          | -0.952                   | 2.5 E-4                | 0.045                  |
| Sn-Cu                 | -0.643                   | 0.9 E-5                | 0.041                  |
| SAC305                | -0.673                   | 1.7 E-5                | 0.059                  |

3.2 Structural analyses
For ternary Sn-9(5Al-Zn) solder alloys, Sn are dominants with some Zn and Al found on the surface of the solder. No new compound formed due to limited solubility of all elements in each other. Sn-Cu consists of $\beta$-Sn and Cu$_6$Sn$_5$ while Ag$_3$Sn was detected for SAC305. The ICDD file no. of 00-004-
0673 and 00-001-0926 matched pure Sn, 00-004-0831 matched pure Zn, 01-089-2837 matched pure Al, 03-065-2303 and 00-045-1488 matched Cu₆Sn₅ and 01-071-0530 matched Ag₃Sn. During the soldering process, Ag combined together with Sn to form Ag₃Sn while Cu₆Sn₅ is a result from precipitation of Cu in Sn matrix [13]. Some Sn peaks decreased due to formation of intermetallic compound that combined with Sn such as Cu₆Sn₅ and Ag₃Sn.

**Figure 2.** XRD profile for as-prepared of SAC305, Sn-Cu and Sn-9(5Al-Zn).

Figure 3. shows the XRD peaks of Sn-9(5Al-Zn), Sn-Cu and SAC305 after polarization in 1 M HCl. The corrosion product of all these three solder alloys only involved SnO, SnO₂ and ZnO. The ICDD file no. for SnO matched with 01-077-2296 and 00-024-1342 while SnO₂ matched with 00-033-1374 and 00-029-1484. As for ZnO, the ICDD file no. matched with 01-075-1533. As expected, no Al by-product were detected due to low amount of this element. Intermetallic compound formed also does not formed new corrosion products that engaging with oxides. It can be concludes that Sn oxide detected for all solders as Sn is the main element in all three solder compositions. ZnO formed as Zn is the first element to dissolve for Sn-9(5Al-Zn). Interestingly, Sn oxides are the dominant corrosion products and aligned with previous report of Mohamed et al. [14]. Formation of SnO₂ shows all the solder already achieved its stable formed [6].

**Figure 3.** XRD profile after polarization of SAC305, Sn-Cu and Sn-9(5Al-Zn) in 1 M HCl electrolyte.
3.3 Morphology analyses

Morphological changes in Sn-9(5Al-Zn) solder before and after polarization showed in Figure 4. Needle-like Zn phase scattered in Sn matrix can be observed before corrosion. However, Al cannot be detected at the lining of Zn phase as it is very small in amount to independently be found on the surface of solder. It is clearly observed there are two distinctive phase between Zn and Sn matrix. After polarization, the surface of Sn-9(5Al-Zn) solder had become rough and small, deep grooves are all over the surface. Zn-rich phase are no longer detected. This groove possibly made from dissolution process of Zn and Sn during polarization. The active materials react with oxide to form metal oxide and deposited on top of the surface in order to protect it from further reaction [15].

![Image](image_url)

**Figure 4.** Microstructure of Sn-9(5Al-Zn) (a) as-prepared,(b) after polarization in 1 M HCl electrolyte.

Morphology of as-prepared Sn-Cu is almost similar to SAC305. The light gray area refers to Sn-matrix while the dark phase refer as Cu₆Sn₅ (Figure 5 and 6). However, the Ag₃Sn phase existed as darker gray area but not dominant on the surface of the SAC305 solder (Figure 6). The morphology of both solder changed after polarization in 1 M HCl electrolyte. The phase that can be found during as-prepared were diminished and replaced with the corrosion products throughout the surface. As predicted, the dissolution process of Sn in both type of solder has resulted in various shape of corrosion product while go through the passivation and pseudopassivation process. Due to random deposition of the by-products, uneven protective layer caused different shape of the corrosion product. This agreed the previous XRD results that protective layer might be build with different Sn oxides of SnO or SnO₂. Worse, continuous attack from Cl- ions enhancing the formation of pitting. If this occurred, Sn chloride by products would be formed. However, in this research, only Sn oxides formed showed the degradation is not very severe. Different shape of corrosion product that formed on top of the surface allow gap to presence in between the corrosion product itself especially for Sn-Cu and SAC305. This is due to direct passivation after activation region. As Sn-9(5Al-Zn) has two stages of passivation, the first passivation layer already closed the gap in between of the corrosion products but reactivation made the second passivation layer to become uneven during deposited. This lead to small grooves formed on the surface of the solder. Compact shape corrosion product is much stable due to small gap and small chances to be attack further by Cl- ions.
Figure 5. Microstructure of Sn-0.7Cu (a) as-prepared,(b) after polarization in 1 M HCl electrolyte.

Figure 6. Microstructure of SAC305 (a) as-prepared,(b) after polarization in 1 M HCl electrolyte.

4. Conclusion
Corrosion properties of Sn-9(5Al-Zn) solder in 1 M HCl electrolyte are very differed in many aspects compared with Sn-Cu and SAC305. Sn-9(5Al-Zn) were prone to corrosion as compared to Sn-Cu based solder due to its larger I_{corr} and low value of E_{corr}. Removal of Zn is more rapid as Zn is easily degraded compared to Sn in the solder system. Structural and morphological results also proved that metal oxide of Sn are dominant on all three types of solder surface. Presence of mixed corrosion products after polarization confirmed that passivation has took place on the surface of solder. Sn-9(5Al-Zn) that has two passivation stages showed less corrosion resistance as compared to SAC305 and Sn-Cu that only consist one passivation region. Therefore, the reliability of Sn-based lead-free solder are significantly affected by the addition of element involved.

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