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Short Communication

Effects of Corrosion on the Shear Strength of Cu/Sn-9Zn/Cu Lap Joints in 3.5 wt. % NaCl Solution

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The effects of corrosion on the shear strength of Cu/Sn-9Zn/Cu lap joints in 3.5 wt. % NaCl solution were investigated. The ultimate shear strength and yield strength of the lap joints decreased by 45% and 36% after immersion, respectively. The ductility of the lap joints also greatly decreased. X-ray diffraction and scanning electron microscopy characterizations of the corroded Cu/Sn-9Zn/Cu lap joints revealed the presence of corrosion byproducts. X-ray diffraction analysis confirmed that these byproducts were ZnO and $ZnCl_2$. Pits and corrosion byproducts also formed on the surface of the corroded lap joints.

Keywords: Corrosion; Cu/Sn-9Zn/Cu lap joints; NaCl; Ultimate shear strength; Yield strength

1. INTRODUCTION

The application of tin-lead solder alloy (63Sn-37Pb) as an interconnecting material in the electronic packaging industry has raised problematic issues such as human health concerns, groundwater pollution, lead poisoning, among others [1]. Hence, "green" electronic products developed by studying Pb-free solders have become suitable alternatives to the Sn-Pb system [2]. Tin-zinc solder alloy (Sn-9Zn) is one such alternative. Sn-9Zn eutectic solder alloy has a melting point of 198 °C, relatively close to that of 63Sn-37Pb solder alloy (183 °C) [3].

Sn-9Zn solder has sufficiently good mechanical properties that are important in terms of reliability [4]. Some of these mechanical properties are ultimate shear strength (USS), yield strength (YS), and ductility [5]. Yoon and Jung [6] reported that the shear strength of Sn-9Zn significantly decreased after aging for an initial 100 hours at all temperatures, and then remained constant with further prolonged aging. However, studies on the shear strength of Sn-9Zn lap joints are very limited.

During its lifespan, solder joints are normally exposed to corrosive media. Prolonged exposure significantly affects the mechanical properties of solder joints, particularly the shear strength. Detrimental effects on the shear strength values greatly affect the reliability and performance of devices. Sodium chloride (NaCl) solution is a common example of corrosive medium that can contribute to such effects. NaCl solution is used to simulate the seawater conditions that electronic devices may be subjected to during marine operation. Li et al. [7] stated that after polarization in 3.5 wt. % NaCl solution, the interfacial adhesion strength of Sn-9Zn-1.5Ag/Cu decreases [8].

The effects of corrosion on the shear strength of Cu/Sn-9Zn/Cu lap joints in 3.5 wt. % NaCl solution were investigated. The objectives were to analyze the effects of corrosion on the USS and YS of Cu/Sn-9Zn/Cu lap joints in NaCl solution, as well as the phase and microstructural changes.

2. EXPERIMENTAL

Sn-9Zn solder alloy was produced by the melting process in a box furnace under an oxygen-free nitrogen environment at 500 °C. The solder alloy was cooled at room temperature and molded into 0.5 mm-thick plates. Solder pellets 5 mm in diameter were produced by a puncher.

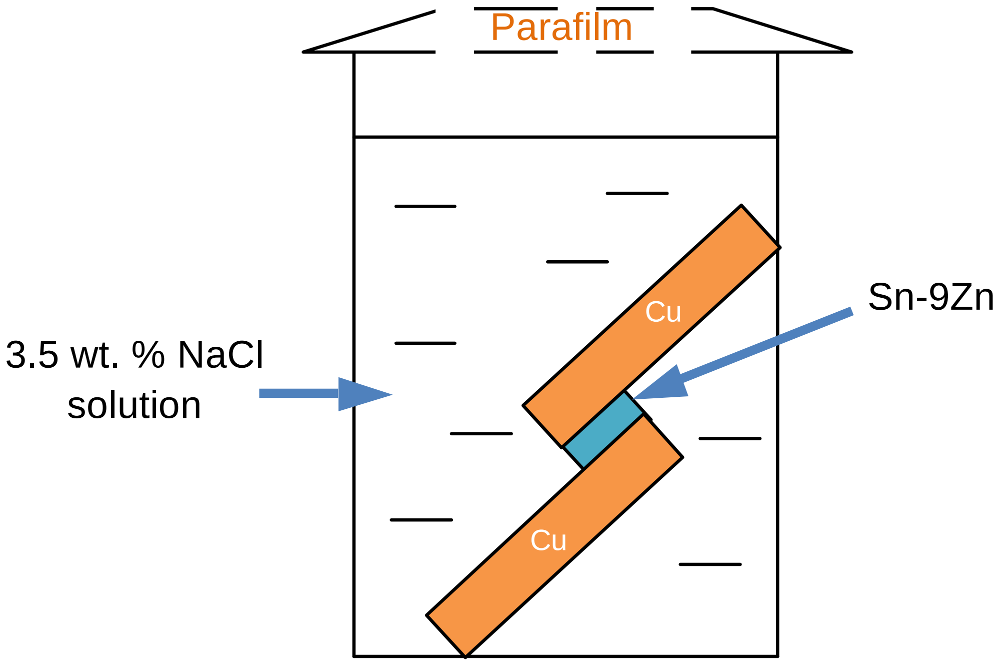

Figure 1. Immersion method for Cu/Sn-9Zn/Cu lap joint in 3.5 wt. % NaCl solution under an open laboratory environment.

A Cu/Sn-9Zn/Cu lap joint was made with two Cu bars (50.0 mm × 5.0 mm × 0.5 mm) and a Sn-9Zn solder pellet. The components were ground and polished using common metallographic practices. Soldering was performed on a hot plate in the presence of a suitable flux. The temperature was maintained above 200 °C for about 30 s, with the highest temperature reaching 220 °C. The soldered joint was left to solidify at room temperature.

Phase determination of the Cu/Sn-9Zn/Cu lap joint was conducted via X-ray diffraction (XRD) using a Bruker AXS D9 diffractometer. A Hitachi TM3000 tabletop scanning electron microscopy (SEM) system was used to identify changes in the lap joint microstructure. The shear strength test of the lap joint was performed using a universal testing machine (INSTRON 5900 Testing System) at room temperature and crosshead speed of 2 mm/min. The USS and YS values were recorded.

Post-corrosion Cu/Sn-9Zn/Cu lap joints were formed by an immersion method. The as-soldered lap joints were immersed in 3.5 wt. % NaCl solution for 28 days. The schematic of the experimental apparatus during immersion is illustrated in Figure 1. After immersion for a certain period, the lap joints were then subjected to the shear strength test and further characterized by XRD and SEM.

3. RESULTS AND DISCUSSION

3.1 Effects of corrosion on the shear strength

Figure 2 shows the stress-strain curves of the shear strength test for Cu/Sn-9Zn/Cu lap joints. Figure 2a depicts the Cu/Sn-9Zn/Cu lap joint before immersion, and Figure 2b presents the lap joint after immersion in 3.5 wt. % NaCl solution. There are three distinct stages observed in Figure 2a: (i) elastic, (ii) strain hardening, and (iii) failure regions. On the other hand, only two regions are seen in Figure 2b: elastic and failure regions.

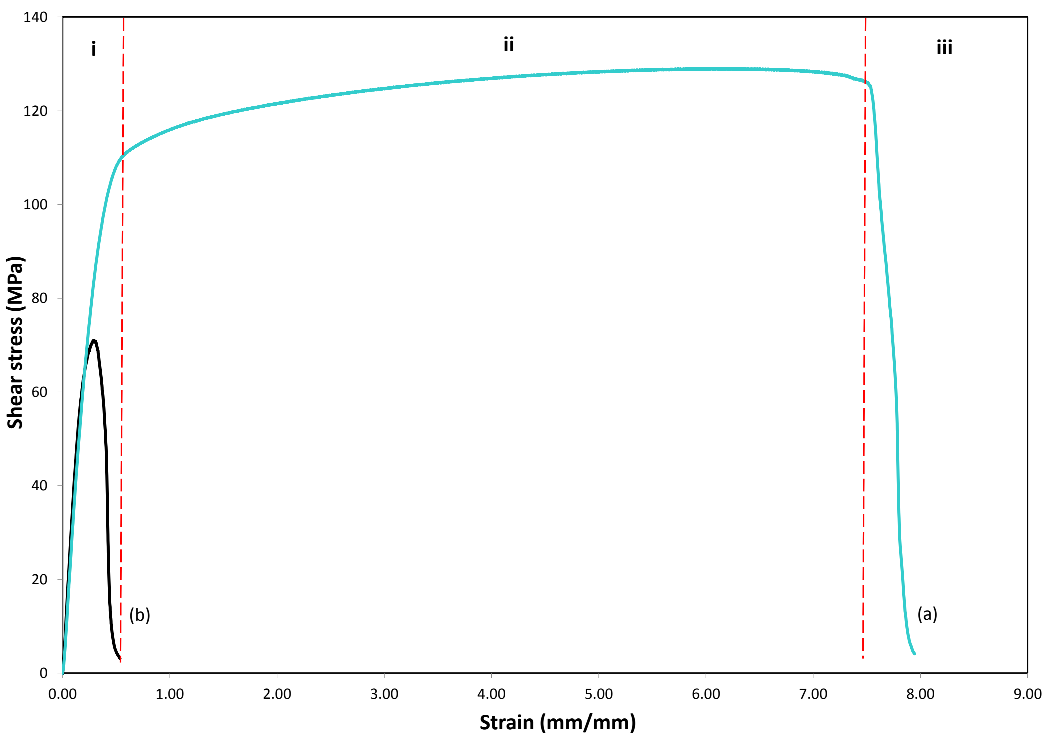

Figure 2. Stress-strain curves of Cu/Sn-9Zn/Cu lap joints (a) before and (b) after immersion for 28 days in 3.5 wt. % NaCl solution.

Based on the obtained curves, the USS and YS of the lap joints are recorded and listed in Table 1. The Cu/Sn-9Zn/Cu lap joint before immersion has the highest USS of 128.5 MPa and YS of 109.58 MPa. Immersion in 3.5 wt. % NaCl solution leads to decreased strength values of the lap joint. After immersion, the USS and YS of the lap joint decreased to 70.97 and 70.32 MPa, respectively.

Table 1. Comparison of shear strength test results of Cu/Sn-9Zn/Cu lap joints before and after immersion for 28 days in 3.5 wt. % NaCl solution.

Immersion period	Ultimate shear strength (MPa)	Yield strength (MPa)	Strain before failure (mm/mm)
Before	128.50	109.58	7.22
After	70.97	70.32	0.29

Notably, the two curves had significantly large different strain values. Figure 2a shows that the strain value before failure is 7.22 mm/mm. After immersion, the strain value is only 0.29 mm/mm. The large strain value in Figure 2a is mainly distributed within the strain-hardening region.

The results show that before immersion, the Cu/Sn-9Zn/Cu lap joint experiences ductile failure, which can be well represented by three stages and the observed large strain-hardening region. During the shear strength test, stresses from opposite directions were applied on the Sn-9Zn solder. Initially, Sn-9Zn solder is ductile; hence, necking occurs slowly across the solder. Fracture occurs in the solder region with the lowest strength [8]. As a result, this particular stage leads to the high values of USS and YS.

The decrease in USS and YS for the Cu/Sn-9Zn/Cu lap joints can be attributed to the corrosion process. The chloride ions released in the solution attacked the exposed surface area of the lap joints. Pit formation and corrosion byproduct formation may have occurred. The stress-strain curve is a typical representation of brittle failure. The formation of pits and corrosion byproducts could have been stress concentration points on the Sn-9Zn solder. Applied stresses on these points may have accelerated the fracture process, resulting in rapid failure. These findings are similar to those of Nazeri et al. [9] for Cu/Sn-9Zn/Cu butt joint in alkaline solution.

3.2 Microstructural analysis

The side-view SEM micrograph of the Cu/Sn-9Zn/Cu lap joint before immersion in 3.5 wt. % NaCl solution is shown in Figure 3a. The Sn-9Zn solder layer is sandwiched between two Cu layers. The surface is smooth and there is no discrete microstructural change on the joint. A very thin layer of different contrast from Cu and Sn-9Zn is observed at the Cu/Sn-9Zn interfaces. Intermetallic compounds were present as a result of its formation during the soldering process.

On the contrary, prominent microstructural changes are observed in the Cu/Sn-9Zn/Cu lap joint after immersion (Figure 3b). First, there are dark pits found in the Sn-9Zn layer and its structure changes from smooth to rough. Deposits of byproducts with different shapes are also widely observed on the surface. Elongated and thick cracks are noticeable throughout the Sn-9Zn layer. Several light-colored regions with smooth structure that closely resemble the Sn-9Zn layer in Figure 3a are also prominent. These regions are the Sn-9Zn solder regions that did not react with the NaCl solution.

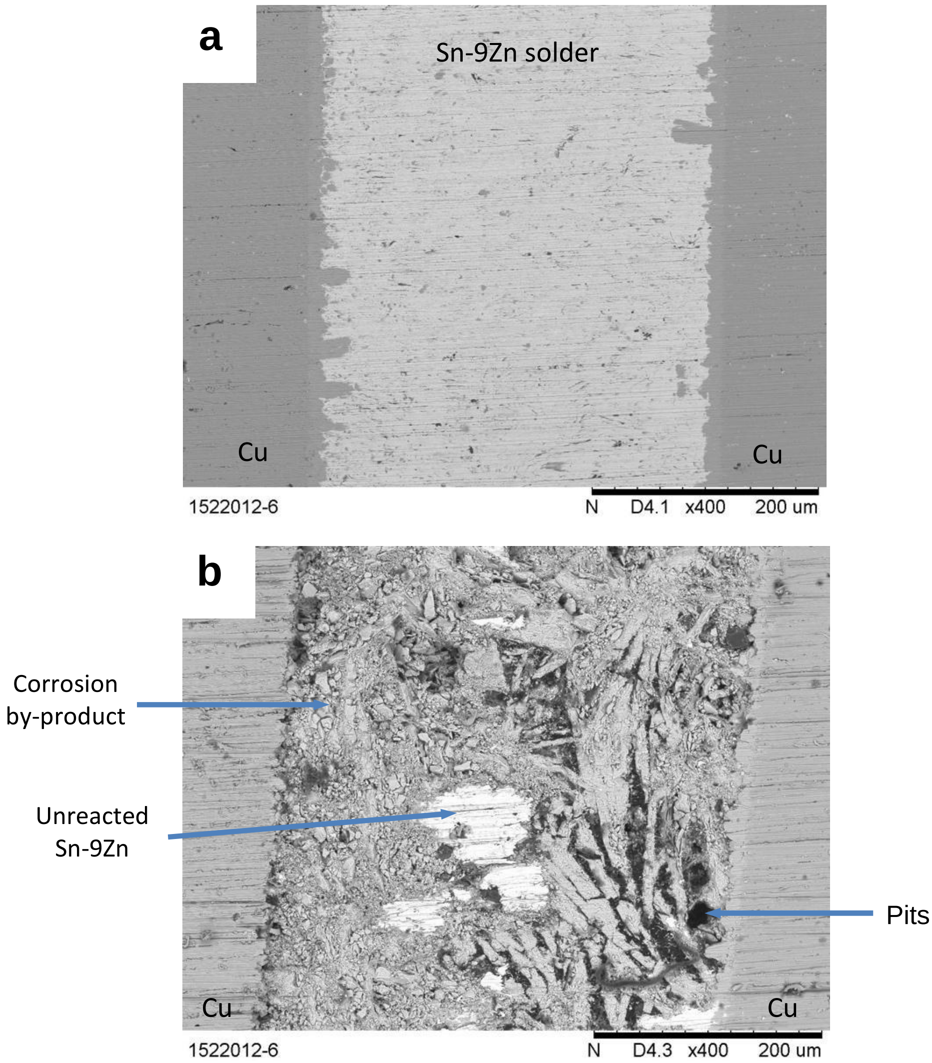

Figure 3. Cross-section micrographs of Cu/Sn-9Zn/Cu lap joint surfaces (a) before and (b) after immersion for 28 days in 3.5 wt. % NaCl solution.

3.3 Phase determination analysis

Figure 4a presents the XRD patterns of the Cu/Sn-9Zn/Cu lap joint before immersion in 3.5 wt. % NaCl solution. The analysis was focused specifically on the sandwiched Sn-9Zn layer. Based on the XRD patterns, phases of Sn and Zn are present in the lap joint. There are six peaks of Sn observed, and there are two peaks of Zn. All Sn and Zn peaks matched ICDD file numbers 00-004-0673 and 00-004-0831, respectively. There are other peaks present that are later identified as the peaks of the intermetallic compounds of the lap joint. Cu_6Sn_5 (00-045-1488) peaks are detected at 30.53°, 31.94°, and 79.38°. There is only one peak detected for Cu_5Zn_8 (00-071-0397), i.e., at 64.43°.

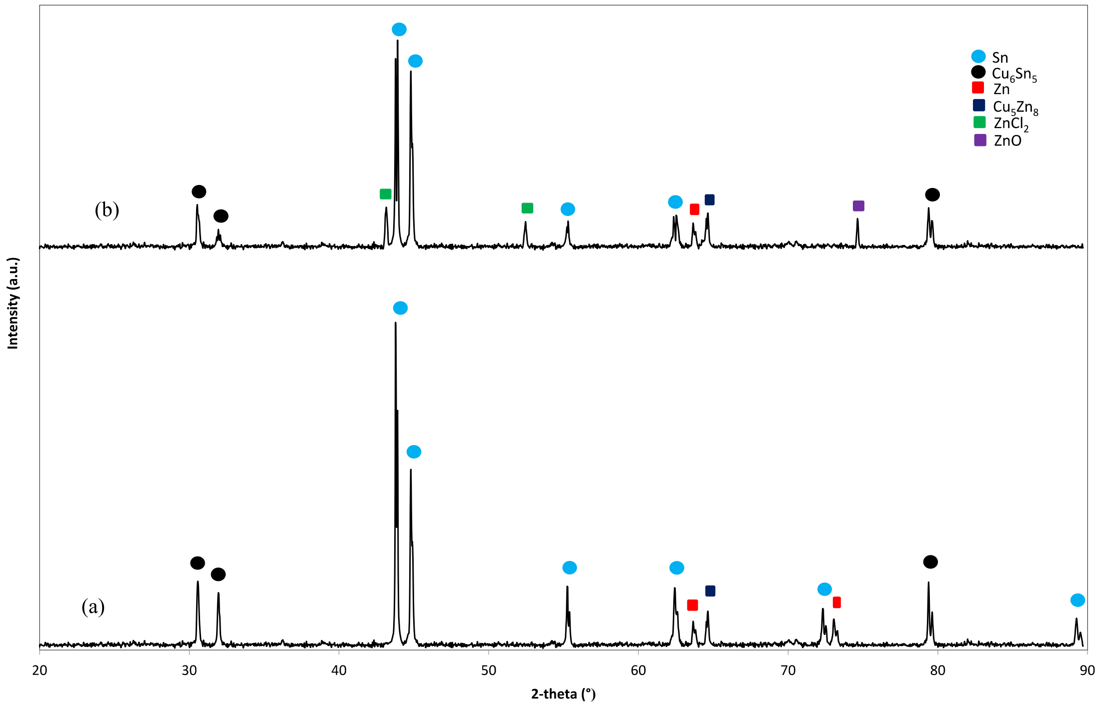

Figure 4. XRD patterns of Cu/Sn-9Zn/Cu lap joints (a) before and (b) after immersion for 28 days in 3.5 wt. % NaCl solution.

Figure 4b shows additional peaks in the XRD patterns of the Cu/Sn-9Zn/Cu lap joint. The peaks are identified as $ZnCl_2$ (43.09° and 52.39°) and ZnO (74.59°). These peaks correspond with ICDD file numbers 01-072-0538 and 01-089-0510 for $ZnCl_2$ and ZnO, respectively. There are several Sn peaks with reduced intensities but not totally removed, as supported by the SEM result for the unreacted region (Figure 3b). The peaks at 72.30° and 89.20° are fully diminished, similar to the Zn peak at 72.54°.

Once the lap joint is immersed in NaCl solution, very distinct microstructural and structural changes are observed. According to Chang et al. [10], pits are generated by the dissolution of $AgZn_3$ and Ag_5Zn_8. However, for this particular case, $AgZn_3$ and Ag_5Zn_8 do not form in the joint; therefore, pit formation may be due to the dissolution of Cu_5Zn_8. Sn-9Zn solder is reportedly sensitive toward pitting corrosion [10].

The deposits found on the lap joint are represented by the corrosion byproducts formed during immersion in 3.5 wt. % NaCl solution. From the Sn-9Zn solder layer, the anodic reaction of Zn constitutes the dissolution of Zn to Zn^{2+}:

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad (1)$$

Later, the cathodic reaction corresponds to the reduction of oxygen [11]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

These ions react on the solder layer surface to form ZnO:

$$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

Zn is much more likely to corrode than Sn because the corresponding Gibbs free energy value of ZnO is much lower than that of SnO [11]. The aggressive chloride ions react with free Zn^{2+} ions to form $ZnCl_2$:

$$Zn^{2+} + 2\ Cl^- \rightarrow ZnCl_2 \quad (5)$$

The formation of these brittle corrosion byproducts may have been the key contributor to the elongated, thick cracks on the solder surface. This observation clearly explains the rapid joint failure and decreased strength values in the shear strength test.

4. CONCLUSION

The corrosion effects on the shear strength of Cu/Sn-9Zn/Cu lap joints in 3.5 wt. % NaCl solution were investigated. The corrosion of lap joints by immersion evidently decreased the USS, YS, and strain values before failure. This result can be explained by the formation of pits and corrosion of byproducts on the surface of Cu/Sn-9Zn/Cu lap joints. These formations served as stress concentration points that were detrimental to the shear strength values of the lap joints. The failure of lap joints changed from ductile to rapid brittle failure.

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