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Investigation of Corrosion Properties of Lead-Free Solder Alloys in 3.5% NaCl Solution

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Abstract: The restriction of lead-based solders due to environmental and health concerns has made the use of lead-free alloys essential in the electronics industry. Among the available alternatives, tin-based systems containing silver and copper have been extensively studied for their potential to provide reliable and sustainable soldering solutions. This study investigates the corrosion behavior of Sn–Ag, Sn–Cu, and Sn–Cu–Ag solder alloys in a 3.5% NaCl solution, simulating chloride-induced conditions commonly encountered by electronic components in humid or coastal environments. The samples were subjected to potentiodynamic polarization tests using a three-electrode system consisting of a saturated calomel electrode (SCE) as reference, a platinum counter electrode, and the solder alloy as the working electrode. The electrochemical results revealed clear distinctions among the tested alloys. The Sn–Cu–Ag alloy exhibited the lowest corrosion current density (4.3×10^{-6} A/cm²) and the most positive corrosion potential (–0.733 V vs. SCE), better corrosion resistance compared to binary Sn–Ag and Sn–Cu systems. Both Sn–Ag and Sn–Cu alloys also achieved current densities around the 10^{-6} A/cm² threshold, which is generally considered acceptable for electronic solder joints, confirming their applicability under mild corrosive conditions. Overall, the results highlight that the Sn–Cu–Ag system offers the most balanced performance and electrochemical durability. The findings contribute to the optimization of lead-free solder materials and support their integration into reliable, long-life electronic assemblies.

Keywords: Soldering, Corrosion, Tin

Introduction

The continuous evolution of environmental regulations and the Restriction of Hazardous Substances (RoHS) directive have led to a global shift toward lead-free solder materials in the electronics industry. Traditional tin–lead (Sn–Pb) solders, despite their excellent wettability, low melting point, and mechanical reliability, have been progressively phased out due to the toxicological risks associated with lead exposure (Farina & Morando, 2015). As a result, tin-based alloys such as Sn–Ag, Sn–Cu, and Sn–Ag–Cu systems have gained prominence as potential replacements owing to their comparable melting characteristics and mechanical stability (Li et al., 2020).

Among these, Sn–Ag–Cu alloys are considered the most balanced alternative due to their near-eutectic composition, good wetting behavior, and reliable electrical performance. The Sn–3.0Ag–0.5Cu alloy, in particular, has become a benchmark material in high-reliability applications such as aerospace and automotive electronics (Chen et al., 2025). However, despite its widespread adoption, the long-term corrosion performance of these alloys in chloride-rich environments remains a key concern, as electronic assemblies often encounter humid or marine conditions that promote electrochemical degradation.

Corrosion in solder alloys generally involves the anodic dissolution of tin and the subsequent formation of corrosion products such as SnO, SnO_2, and $Sn_3O(OH)_2Cl_2$, depending on the presence of chloride ions in the environment (Li et al., 2020). Studies have shown that the corrosion resistance of lead-free alloys is highly

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sensitive to their microstructural features—particularly the morphology and distribution of intermetallic compounds (IMCs) such as Ag_3Sn and Cu_6Sn_5 (Mohanty & Lin, 2007). Fine and uniformly dispersed IMCs can promote the stability of passive films, whereas coarse or plate-like morphologies may act as initiation sites for localized corrosion (Tunthawiroon & Kanlayasiri, 2019).

The effect of silver and copper concentration on the corrosion performance of Sn-Ag-Cu alloys has been explored in various works. For instance, increasing Ag content beyond 2 wt.% enhances passivation and refines the eutectic structure, though excessive Ag promotes large Ag_3Sn platelets that deteriorate mechanical ductility (Rosalbino et al., 2008). On the other hand, Cu additions contribute to improved passivity and the formation of compact corrosion layers, reducing ion migration and pitting susceptibility (Farina & Morando, 2015).

This study focuses on the corrosion characteristics of Sn–Ag, Sn–Cu, and Sn–Ag–Cu lead-free solder alloys under 3.5% NaCl conditions, employing potentiodynamic polarization techniques. The objective is to establish a comparative understanding of their electrochemical behavior, identify microstructural factors governing corrosion resistance, and support the ongoing optimization of environmentally compliant and durable solder materials.

Method

In this study, commercially available and previously homogenized Sn–Ag, Sn–Cu, and Sn–Ag–Cu lead-free solder alloys were used (Table 1). Each sample surface was mechanically abraded using 1200-grit SiC sandpaper to remove surface oxides and irregularities. Following this, polishing was performed with 6 µm and 3 µm diamond suspensions to obtain a mirror-like finish suitable for electrochemical analysis. After surface preparation, all specimens were rinsed sequentially with distilled water and ethanol in an ultrasonic bath, then dried with clean air before testing.

Table 1. Chemical composition of the tested solder alloys (wt.%).

Alloy Code	**Sn (wt.%)**	**Ag (wt.%)**	**Cu (wt.%)**
Sn–Ag	96.5	3.5	–
Sn–Cu	99.3	–	0.7
Sn–Cu–Ag	96.5	3.0	0.5

To simulate a corrosive environment and investigate the influence of chloride ions on localized corrosion, a 3.5 wt.% NaCl solution was prepared as the main electrolyte. Chloride ions (Cl^-) are known to promote pitting corrosion, which poses a significant threat to electronic solder materials. To ensure adequate ionic conductivity within the test medium, 0.1 M K_2SO_4 was added to the solution. Additionally, 0.1 M K_2HPO_4 was introduced to stabilize the pH and provide a buffering effect. The mixture was continuously stirred on a magnetic stirrer to achieve a homogeneous solution. The pH of the prepared electrolyte was carefully monitored using a calibrated pH meter and adjusted to 7.0 ± 0.1 with H_2SO_4. All experiments were conducted at room temperature. Electrochemical corrosion tests were carried out using a standard three-electrode system in a single-compartment electrochemical cell. A saturated calomel electrode (SCE) served as the reference electrode, a platinum electrode as the counter electrode, and the prepared solder alloy as the working electrode. The exposed surface area of the working electrode was 0.785 cm².

Prior to each measurement, the electrolyte was deaerated with argon gas to minimize oxygen interference. Potentiodynamic polarization curves were obtained using a GAMRY Interface 1010B potentiostat, controlled by dedicated computer software. After reaching a stable open-circuit potential, the polarization scan was initiated from –0.5 V to +1 V (vs. SCE) at a rate of 1 mV/s. Throughout the experiment, both potential and current density values were continuously recorded. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were determined using Tafel extrapolation from the polarization curves.

Results and Discussion

Potentiodynamic polarization tests were performed to evaluate the corrosion behavior of Sn–Ag, Sn–Cu, and Sn–Ag–Cu solder alloys in the prepared 3.5 wt.% NaCl electrolyte. The corrosion performance of these alloys was primarily assessed through their electrochemical response in 3.5 wt.% NaCl solution. As summarized in Table 2, the measured corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}) indicate that all three solder systems exhibited similar tendencies toward anodic dissolution, with small variations depending on alloy composition.

Table 2. Electrochemical parameters (E_{corr} and I_{corr}) of Sn–Ag, Sn–Cu, and Sn–Cu–Ag solder alloys obtained from potentiodynamic polarization measurements.

Alloy Composition	**Ecorr(V vs. SCE)**	**Icorr(A·cm^{-2})**
Sn–Ag	–0.753	7.24×10^{-6}
Sn–Cu	–0.748	8.94×10^{-6}
Sn–Cu–Ag	–0.733	4.30×10^{-6}

The polarization curves, illustrated in Figure 1, represent the potentiodynamic test results obtained for each alloy system, while Figure 2 presents an enlarged view of the open-circuit potential (OCP) region showing the detailed potential stabilization prior to anodic polarization.

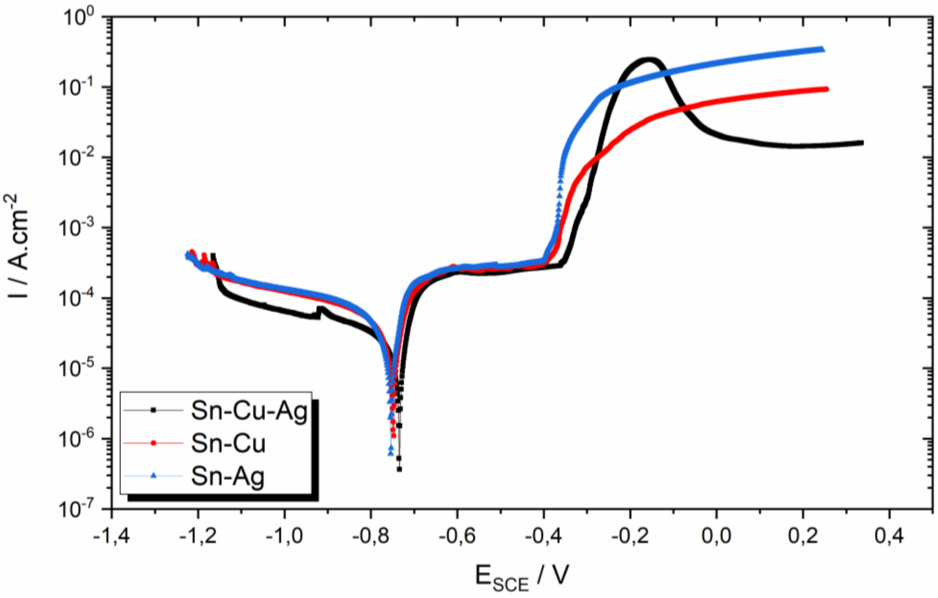

Figure 1. Potentiodynamic polarization curves of Sn–Ag, Sn–Cu, and Sn–Ag–Cu solder alloys in 3.5 wt.% NaCl solution.

All samples exhibited active–passive transitions typical of tin-based alloys exposed to chloride-containing environments. The Sn–Cu–Ag alloy displayed a more positive corrosion potential ($E_{corr} \approx -0.733$ V vs. SCE) and lower corrosion current density ($I_{corr} \approx 4.3\times10^{-6}$ A/cm²) compared with the binary Sn–Ag and Sn–Cu systems. This indicates a lower corrosion rate and better electrochemical stability under the tested conditions. These results align with those reported by Mohanty and Lin (2007), who observed improved passivation behavior in Sn–Ag–Cu systems due to the formation of stable SnO and SnO_2 surface films.

The Sn–Ag and Sn–Cu alloys showed close potential values (–0.753 V and –0.748 V, respectively), suggesting comparable thermodynamic behavior in chloride-containing environments. However, the slightly higher Icorr value observed for Sn–Cu (8.94×10^{-6} A·cm⁻²) implies a faster dissolution rate than Sn–Ag (7.24×10^{-6} A·cm⁻²). This difference can be explained by the galvanic interaction between the β-Sn matrix and the Cu_6Sn_5 intermetallic compound, which promotes localized anodic activity (Farina & Morando, 2015). In contrast, Sn–Ag exhibits partial passivation due to Ag_3Sn formation, though local micro-galvanic cells between Ag-rich and Sn-rich regions may still initiate minor pitting events (Tunthawiroon & Kanlayasiri, 2019).

The Sn–Cu–Ag alloy presented a more positive E_{corr} (–0.733 V) and the lowest I_{corr} (4.30×10^{-6} A·cm⁻²), indicating a more stable passive behavior. The improved stability is attributed to the combined influence of Ag and Cu, which enhance electrochemical homogeneity and facilitate the formation of a more protective oxide film. These results are consistent with previous findings that emphasize the effect of chloride ions on passive film breakdown. As reported by Pu et al. (2024) and Li et al. (2020), Cl^- ions interact with surface oxides to form soluble complexes such as $SnCl_2$ and $Sn_3O(OH)_2Cl_2$, leading to localized corrosion. Nevertheless, the alloys tested here maintained passivation trends, suggesting that chloride attack was mitigated by the inherent tin-oxide layer formed during exposure.

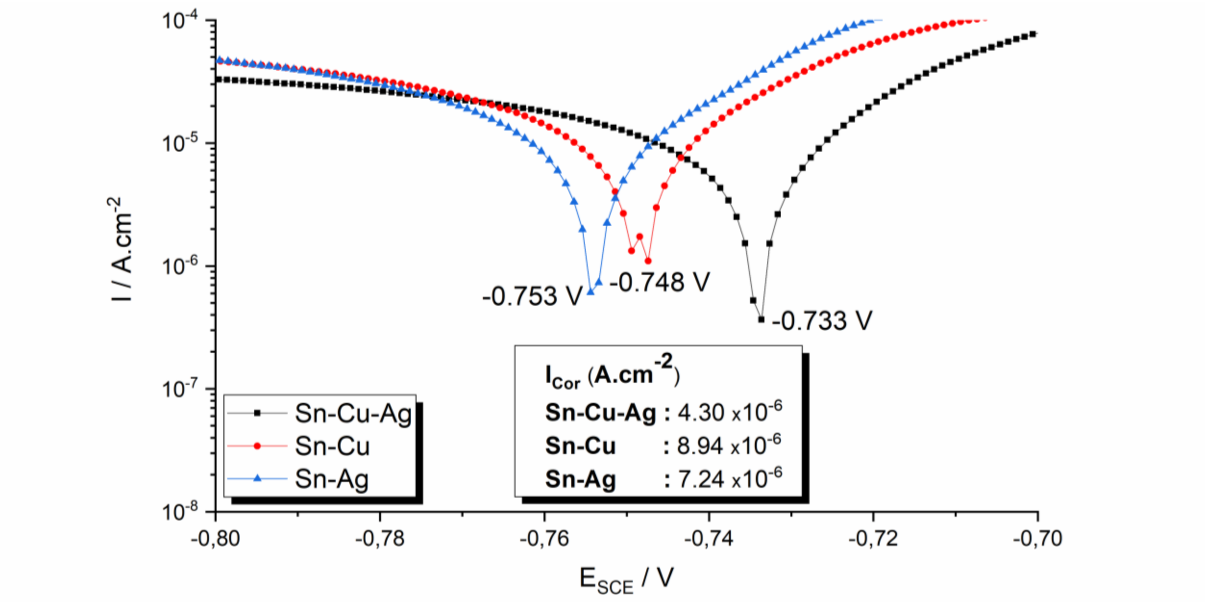

Figure 2**.** Enlarged view of the open-circuit potential (OCP) region of the polarization curves.

Conclusion

This study evaluated the electrochemical corrosion behavior of Sn–Ag, Sn–Cu, and Sn–Cu–Ag lead-free solder alloys in a 3.5 wt.% NaCl electrolyte using potentiodynamic polarization analysis. The results demonstrated that all three solder systems exhibited passivation behavior typical of tin-based alloys in chloride-containing environments. Among the tested compositions, Sn–Ag and Sn–Cu alloys showed similar thermodynamic tendencies toward anodic dissolution, though the Sn–Cu alloy recorded a slightly higher corrosion current density, indicating a somewhat faster dissolution process. The differences in their corrosion performance were mainly attributed to the galvanic interactions between the β-Sn matrix and respective intermetallic phases. The Sn–Cu–Ag alloy presented a more positive corrosion potential and the lowest corrosion current density, suggesting enhanced passivity and improved stability of the surface oxide film. This behavior can be ascribed to the combined influence of Ag and Cu, which promotes a more homogeneous electrochemical response.

Overall, the findings confirm that the Sn–Cu–Ag system offers a more favorable balance of corrosion resistance and environmental compliance compared to binary tin-based solders. These outcomes contribute to the broader understanding of lead-free solder reliability under chloride-induced corrosion conditions and provide valuable insight for future material selection and design in electronic applications.

Scientific Ethics Declaration

* The author declares that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the author.

Conflict of Interest

* The author declares no conflicts of interest

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