



## The role of Zn precipitates and Cl<sup>-</sup> anions in pitting corrosion of Sn–Zn solder alloys



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### ABSTRACT

Electrochemical corrosion behavior of Sn–Zn solder alloys in aerated and quiescent 0.5 M NaCl solution was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques, aiming to assess the role of Zn precipitates and Cl<sup>-</sup> anions in pitting corrosion. The results reveal that increasing in Zn contents leads to increasing in pitting susceptibility, ascribed to the coarsening Zn precipitates with larger intergranular boundaries between Zn-rich precipitates and Sn matrix. The EIS results provide a quantitative description of the electrochemical interface behavior. The mechanism of pitting and the role of Cl<sup>-</sup> anions are discussed.

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### 1. Introduction

The Sn–Pb solders, due to its low cost, effective solderability and proficient mechanical properties, have been extensively used in the interconnection and packaging of electronic products for decades. However, with increasing environmental and health concern over the toxicity of Pb, alternative lead-free solders are required [1–3]. Heretofore, a variety of lead-free solder alloys, including Sn–Zn, Sn–Ag, Sn–Cu and Sn–Bi binary alloys as well as certain ternary and quaternary alloys, have been proposed as alternatives of the conventional Pb-containing solders. Among them, eutectic Sn–9 wt.%Zn alloy is regarded as one of the most promising candidates due to its low melting temperature, decent mechanical properties and low cost [2,4–6].

In general, solders used in electronic packaging components could be exposed directly to air moisture or aggressive medium (e.g. Cl<sup>-</sup>) in industrial environments. This will, unquestionably, increase the corrosion susceptibility of the solder materials and deteriorate their long-term reliability [1,7]. Especially, Sn–Zn alloys are susceptible to corrosion due to the chemical and metallurgical activity of Zn [4]. Thus, understanding the corrosion mechanism of

Sn–Zn alloys is an urgent issue for their practical application as lead-free solders.

Heretofore, the corrosion behavior of lead-free solder alloys in aqueous solution has been extensively investigated [7–13]. Chang et al. [14] studied the electrochemical behavior of the Sn–9Zn–xAg lead-free solders in a 3.5 wt.% NaCl solution and found that Ag addition enhanced the corrosion resistance of the Sn–9Zn solder. Mohanty and Lin [15–17] reported a series of investigations on electrochemical behavior of the five elements Sn–8.5Zn–Ag–Al–Ga alloys in 3.5% NaCl solution. They suggested that the five elements solder exhibited better corrosion resistance compared with Sn–8.5Zn alloy. However, there are few works on the corrosion behavior of Sn–Zn solder base with varying Zn contents, especially in aggressive chloride solution. Moreover, pitting corrosion of the Sn–Zn solders has scarcely been considered yet, although pitting is of the most common cause of corrosion failure in industry and has been studied over several decades [18–25]. In fact, when exposed to an aggressive environment (e.g. in the presence of halide ions), some passive metals or alloys (e.g. Ni and Ni–Cr alloys) are prone to pitting corrosion, although they exhibit decent resistance to general corrosion [26]. Thus, the knowledge of pitting corrosion is essentially required to assess the reliability of Sn–Zn solders from the viewpoint of corrosion, and can also provide a reference for further study aiming to improve their corrosion resistance.

On the other hand, conventional electrochemical measurement (e.g. potentiodynamic polarization), seems insufficient to quantita-

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tively evaluate the corrosion process with respect to the electrochemical interface. In view of this, electrochemical impedance spectroscopy (EIS) has emerged as a more convincing tool [27–32]. EIS allows continuous monitoring of the corrosion process without obviously accelerating the corrosion reaction, and it can provide enough insight into the dielectric behavior, reactions and mass transport across the electrochemical interface, with a well-defined equivalent circuit (EC). Furthermore, this technique is quite sensitive to evolution of resistive and capacitive behavior of the electrochemical interface, regarded as a more effective method for studying the localized corrosion (pitting) [33].

The present work, therefore, aims to provide a fundamental understanding of the pitting corrosion of Sn–Zn solder alloys in aerated and quiescent 0.5 M NaCl solution. Experiments were performed by means of EIS and potentiodynamic polarization on three representative Sn–Zn alloys to assess the role of Zn precipitates and the Cl<sup>−</sup> anions in pitting susceptibility.

## 2. Experimental procedures

### 2.1. Materials preparation

Three representative Sn–Zn solder alloys, i.e. Sn–6.5 wt.%Zn (hypoeutectic), Sn–9 wt.%Zn (eutectic) and Sn–12 wt.%Zn (hyper-eutectic), were prepared from pure metals (Sn and Zn ingots with purity of 99.9%, Senju Metal Co., Ltd. Japan). Hereafter, the composition unit ‘wt.%’ is omitted. The ingots were weighed and melted at 450 °C for 4 h in an electromagnetic induction quartz tube under Argon atmosphere to prevent oxidation of the alloys. The melts were then casted at about 300 °C in a quartz tube mold with a diameter of 7 mm, followed by natural cooling in air. The as-casted alloys were homogenized at 150 °C for 20 h. The chemical compositions of the Sn–Zn alloys were investigated using inductively coupled plasma atomic emission spectrometry (ICP-AES) and the results are shown in Table 1. The microstructures of the prepared alloys prior to electrochemical measurements were characterized using Field Emission-Scanning Electron Microscope (FE-SEM, Hitachi SU8020, Japan).

Specimens of  $\phi$  7 mm  $\times$  4 mm in size were cut out from the prepared alloys. Al wires covered by a plastic insulating tube were soldered to the specimens at the opposite face of the blocks to the working surface. The soldered alloys were mounted with epoxy resin twice to alleviate crevice corrosion. The working surface was mechanically ground with successive silicon carbide paper from 400 to 4000 grit and polished with 0.05  $\mu$ m Al<sub>2</sub>O<sub>3</sub> powder suspensions to obtain a mirror like surface. The coupons were then ultrasonically cleaned with distilled water and dried with high pressure air.

### 2.2. Electrochemical measurements

A conventional three-electrode cell configuration was employed to perform the electrochemical measurements. A Pt spiral wire was used as the counter electrode, and the reference electrode used in this study was Ag/AgCl electrode saturated with KCl. The alloy, as the working electrode, was positioned into the cell filled with 0.5 M NaCl solution at room temperature (22  $\pm$  2 °C). The NaCl solution was prepared using analytical grade chemicals and distilled

water, and was aerated by direct contact with the laboratory atmosphere. Working surface of the electrode exposed to the solution was approximately 0.384 cm<sup>2</sup>. The distance between the working electrode and the reference electrode was kept less than 2.5 mm. All the electrochemical measurements were conducted using a Solartron 1287-S electrochemical interface and a Solartron 1255B-S frequency response analyzer controlled by a personal computer. Prior to any measurement, the working electrode was immersed in the identical solution with a volume of 100 ml for desired time.

EIS data as a function of immersion time was obtained at the open circuit potential (OCP) over a frequency range from 100 kHz to 100 mHz, with a potential amplitude of 10 mV RMS (root-mean-square) as the applied sinusoidal perturbation. The frequency values were spaced logarithmically (at seven steps per frequency decade). Prior to the EIS tests, the working electrode was immersed in the tested solution for 90 min at the OCP. Potentiodynamic polarization measurements were carried out immediately after EIS measurements in case of 2 h immersion, at a voltage scanning rate of 1 mV/s. The acquired impedance spectra and polarization curves were then curve-fitted and analyzed using ZView (version 3.3d) and CView (version 3.3c) softwares, respectively, to obtain information about the electrochemical interface behavior and to determine the fundamental electrochemical parameters. Duplicate tests were performed to verify reproducibility.

The morphology and chemical compositions of the corrosion products formed on the alloys after the electrochemical measurements, were characterized using FE-SEM coupled with Energy Dispersive X-ray Spectroscopy (EDX). The samples for cross-section observation after the electrochemical measurements were prepared by ion milling (IM4000, Hitachi Hightech Co., Ltd, Japan).

## 3. Results

### 3.1. Microstructures of Sn–Zn alloys

Fig. 1 shows the representative microstructures of Sn–Zn solder alloys prior to electrochemical measurements. All alloys present a typical two phases structure with a matrix of  $\beta$ -Sn wherein needle-like Zn-rich precipitates are dispersed. For hypoeutectic Sn–6.5Zn alloy (Fig. 1a), fine Zn-rich precipitates segregate in the  $\beta$ -Sn matrix to form part of eutectic appearance and  $\beta$ -Sn islands can be clearly observed. This is similar to that reported in the literature [34]. As shown in Fig. 1b, the Sn–9Zn alloy exhibits a typical characterization of eutectic structure with some larger Zn-rich precipitates distributed in the  $\beta$ -Sn matrix. Further increasing the amount of Zn up to 12 wt.% results in much more and coarser Zn-rich precipitates (Fig. 1c). These coarser Zn-rich precipitates are detrimental to mechanical reliability of the joints because of more defects (e.g. dislocation) accumulation and thus increasing susceptibility to voids formation [35].

### 3.2. Electrochemical impedance spectroscopy

Fig. 2a and b shows the Nyquist impedance plots and Bode plots for Sn–6.5Zn solder alloy recorded as a function of immersion time

**Table 1**  
Chemical compositions of the three Sn–Zn solder alloys (wt.%) measured by ICP-AES.

Solder alloy	Sn	Zn	Sb	Bi	Fe	Ag	In	Pb
Sn–6.5Zn	Bal.	6.38	0.0059	0.0038	0.0021	0.0002	0.0025	0.016
Sn–9Zn	Bal.	9.00	0.0055	0.0048	0.0019	0.0003	0.0024	0.016
Sn–12Zn	Bal.	11.86	0.0052	0.0048	0.0018	0.0003	0.0022	0.015

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