

CORROSION OF CANDIDATE LEAD-FREE SOLDER ALLOYS IN SALINE SOLUTION

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Abstract

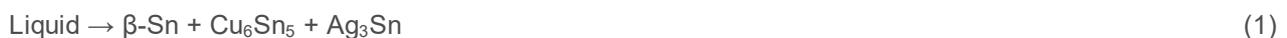
In the present work the corrosion resistance of candidate lead-free solder alloys in simulated seawater conditions was investigated. Four different alloys were studied: Sn-0.7Cu, Sn-3.5Ag, Sn-0.3Ag-0.7Cu and Sn-3.5Ag-0.7Cu (composition in wt.%). The alloys were prepared by induction melting from high purity Sn, Ag and Cu lumps. Each alloy was heterogeneous as it was found to consist of β -Sn and different binary intermetallic compounds. The alloys were corrosion-monitored in 3.5 wt.% NaCl aqueous solution at 21 °C. The electrochemical polarization was conducted in a standard 3-electrode cell provided by Sensortechnik Meinsberg Ltd. The potential-current density curves were measured by using a PGU 10V-1A-IMP-S potentiostat/galvanostat (Jaissle Electronic Ltd., Germany). The corresponding corrosion potentials and corrosion rates were determined by Tafel extrapolation of the experimental polarization curves. The effects of chemical composition and sample microstructure have been evaluated. Conclusions for the solder alloy corrosion resistance in humid environments are provided. The local nobility of individual IMCs is discussed. The results can be used as a guideline for selecting the proper lead-free solder composition for microelectronic applications.

Keywords: Solder, corrosion, intermetallic compound.

1. INTRODUCTION

Soldering is a metallurgical joining technique that uses a filler metal - the solder - to join two metal substrates. Solder is a crucial component of electronic assembly. It provides the electrical, thermal and mechanical continuity [1]. The traditional solders used for decades have been Sn-Pb eutectic and near eutectic compositions. These lead-based alloys have several advantages, including low melting point of the binary eutectic and low surface tension facilitating substrate wetting [1]. Nevertheless, health and environmental concerns with lead limit their practical use [2]. Lead is a toxic element that is known to produce various adverse health effects. Its accumulation in human body may lead to disorders in nervous and reproductive systems and result in a serious retardation of neurological and physical development. Lead also causes cognitive and behavioral changes and reduces the production of hemoglobin resulting in anemia and hypertension. To avoid these serious health problems, a European Union directive 2011/65/EU Restriction of the use of hazardous substances in electrical and electronic equipment (RoHS EEE) has been launched [3]. This directive is designed to restrict the use of lead in industry and promote the use of green environmentally friendly materials.

Eutectic and near-eutectic Sn-Ag-Cu (SAC) alloys are candidate lead-free solder alloys. These materials are attractive alloys for soldering since they have a high strength, high fracture toughness and high electrical conductivity. A number of experimental studies have been devoted to the description of the phase equilibria of these systems [4-6]. The ternary eutectic has a composition close to 3.5 wt.% Ag, 0.9 wt.% Cu, 95.6 wt.% Sn. The corresponding invariant reaction can be given by the following equation [4]:



Upon cooling below the eutectic temperature, the beta phase of tin and two intermetallic compounds, Cu_6Sn_5 and Ag_3Sn , are formed.

In many industrial applications, the electronic equipment is exposed to corrosive environment such as moisture or aggressive chemicals. The ability to withstand these conditions is crucial for the electronic device reliability

and long term performance. The electrical connection of solder with metallic substrate creates a potential for galvanically induced corrosion. Furthermore, the alloy degradation may also occur due to an electrical potential difference between different alloy phases. Intermetallic compounds (IMCs) are introduced in lead-free solder alloys either as a result of their chemical composition or due to specific solder-substrate interactions [7]. The local nobility of IMC may result in an anodic dissolution of the surrounding metal matrix during exposure to humid environments (soil, underground water, seawater).

In the present work, 4 different lead-free solder alloys have been tested - Sn-0.7Cu, Sn-3.5Ag, Sn-0.3Ag-0.7Cu and Sn-3.5Ag-0.7Cu (composition in wt.%). These alloys are candidate materials for lead-free soldering. The corrosion performance of the alloys was investigated in a simulated sea water environment (3.5 wt.% sodium chloride solution). The results can serve as a guideline for choosing the proper solder composition for underwater and marine electronic devices.

2. MATERIAL AND METHODS

The alloys were prepared by controlled melting of Ag, Cu and Sn lumps (purity of 99.99 wt.%). Chemical compositions of the alloys are provided in **Table 1**. The weighed amounts of the metals were placed in a ceramic crucible and positioned inside a vacuum induction furnace. The furnace chamber was evacuated and purged with argon (purity of 6N). The melting was conducted at ~ 700 °C. The molten alloys were homogenized by mechanical stirring with quartz-glass rod. The melting was repeated several times. After solidification, cylindrical samples (30 mm diameter, 10 mm height) were made. The samples were mechanically polished with 1 micron diamond paste.

Table 1 Chemical compositions of lead-free solder alloys

Alloys	Sn (wt.%)	Ag (wt.%)	Cu (wt.%)
Sn	99.99	-	-
Sn-0.7Cu	99.32	-	0.68
Sn-3.5Ag	96.92	3.08	-
Sn-0.3Ag-0.7Cu	99.01	0.41	0.58
Sn-3.5Ag-0.7Cu	96.36	3.05	0.59

The corrosion behavior of lead-free solder alloys was investigated by potentiodynamic polarization at room temperature (21±2 °C) [8]. The polished sample surfaces were subjected to an electrochemical polarization in a standard 3-electrode corrosion cell. The working electrode was the solder alloy with an exposed surface area of approximately 536 mm². Platinum foil (400 mm²) was used as the counter electrode. A saturated silver chloride electrode (Ag/AgCl) served as the reference electrode during measurements. The scheme of the corrosion cell is provided in **Fig. 1**.

The corrosion experiments were carried out in an aqueous NaCl solution (0.6 mol·dm⁻³) at room temperature. The electrolyte was prepared by dissolving a weighed amount of NaCl in de-ionized water. A PGU 10V-1A-IMP-S potentiostat/galvanostat (Jaissle Electronic Ltd., Germany) was used to polarize the working electrode and monitor the progress of the reaction. The open circuit potential (OCP) of each alloy was measured first, after 20 minutes of sample immersion in the electrolyte.

The polarization experiments were carried out in a positive direction at potentials between -1000 and +1000 mV (Ag/AgCl). A constant scan rate of 2 mV/s was employed during measurements. Each experiment was repeated twice to check for the reproducibility.

The sample microstructures before and after corrosion testing were investigated by an optical microscope (Zeiss NEOPHOT 2).

The phase occurrence after corrosion was investigated by X-ray Panalytical Empyrean PIXCel 3D diffractometer with Bragg-Brentano geometry (XRD). The instrument was working with a $\text{CoK}_{\alpha 1,2}$ radiation beam. The X-ray radiation beam was generated at 40 kV and 40 mA. The sample diffraction patterns were measured between 20° and 140° (2-theta) at room temperature. The phases were assigned by using the PDF database ICSD FIZ Karlsruhe 2011-1.

3. RESULTS AND DISCUSSION

The microstructures of the alloys are presented in Figs. 2 and 3.

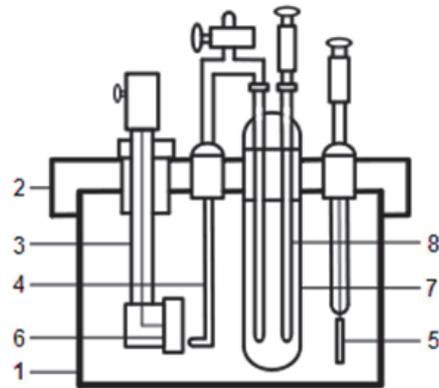


Fig. 1 Corrosion cell for potentiodynamic measurements: 1 - Glass container, 2 - Lid, 3 - Sample holder, 4 - Haber-Luggin capillary, 5 - Counter electrode Pt, 6 - Working electrode, 7 - Salt bridge, 8 - Reference electrode

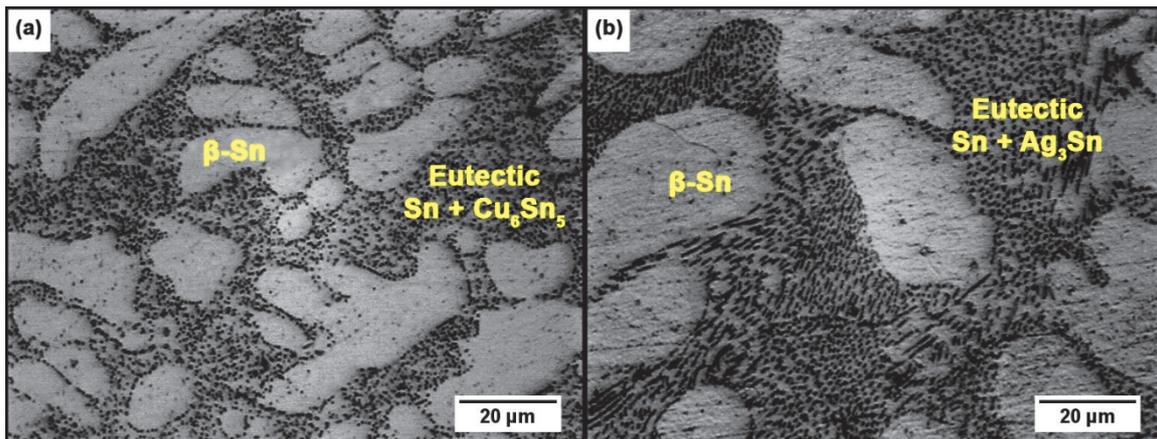


Fig. 2 The microstructure of lead-free solder alloys (a) Sn0.7Cu, (b) Sn3.5Ag

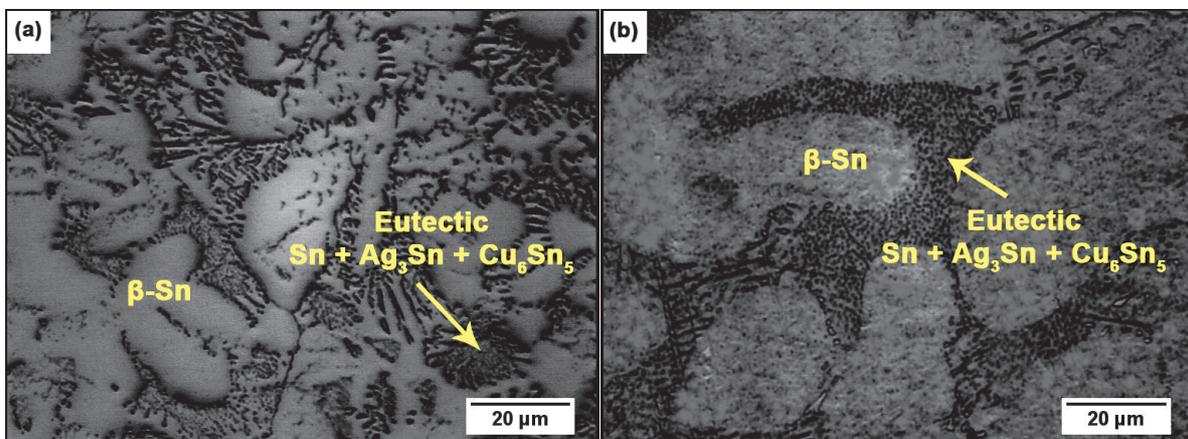


Fig. 3 The microstructure of lead-free solder alloys (a) Sn0.3Ag0.7Cu, (b) Sn3.5Ag0.7Cu.

In these figures the light regions represent the β -Sn grains. The dark regions represent the eutectic. The Sn-0.7Cu alloy is composed of β -Sn and a binary eutectic (**Fig. 2a**). The binary eutectic of the Sn-0.7Cu alloy is composed of Cu_6Sn_5 and β -Sn. The microstructure of the alloy Sn-3.5Ag is composed of Sn-rich dendrites and a eutectic (**Fig. 2b**). The binary eutectic of the Sn-3.5Ag alloy is composed of Ag_3Sn and β -Sn. The ternary Sn-0.3Ag-0.7Cu and Sn-3.5Ag-0.7Cu alloys are composed of β -Sn and a ternary eutectic (**Fig. 3**). The ternary eutectic is composed of β -Sn and Cu_6Sn_5 and Ag_3Sn intermetallic phases.

Corrosion resistance of the solders was tested in a NaCl solution to simulate real environmental conditions the solder may experience during service or storage. An open circuit potential was measured first, immediately after sample immersion in the electrolyte. The OCP values are shown in **Fig. 4**.

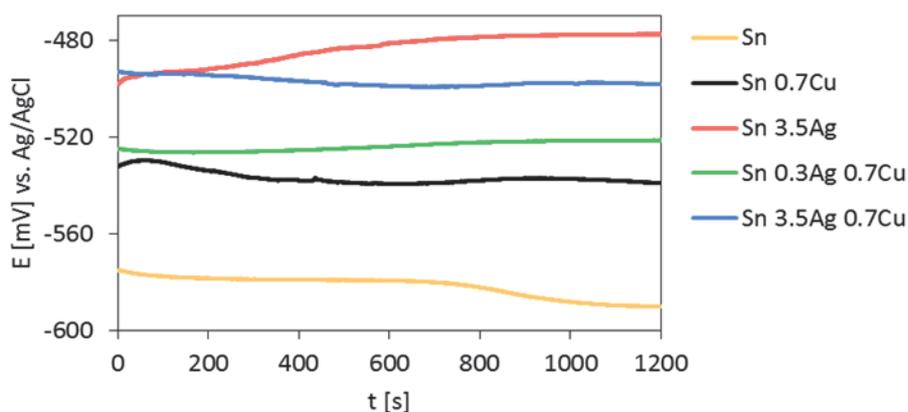


Fig. 4 Open circuit potential (OCP) of lead-free solders

The OCP of the samples was relatively stable over time (**Fig. 4**). In some cases, an intermediate decrease or an increase was observed which was, however, followed by stabilization within 10 min of sample immersion in the electrolyte. The OCP values, measured after 20 minutes of alloy stabilization in corrosion medium, increase in the following order:

$$\text{Sn} < \text{Sn-0.7Cu} < \text{Sn0.3Ag0.7Cu} < \text{Sn3.5Ag0.7Cu} < \text{Sn3.5Ag} \quad (2)$$

These results indicate that the solder corrosion resistance increases with increasing transition metal concentration. The highest OCP is observed for Sn-3.5Ag and Sn-3.5Ag-0.7Cu alloys respectively. The lowest OCP is observed for Sn. The alloys corrosion resistance increases with increasing Ag concentration. This observation is in accordance with the higher standard electrode potential of Ag compared to Sn.

Ag and Cu are cathodic with respect to Sn. As such, these elements may promote the anodic dissolution of the solder matrix. The difference in electro-motoric forces between Sn and Ag_3Sn is large [9]. Therefore, the Sn corrosion is likely to take place because of the electrochemical coupling between these two phases. In order to investigate the corrosion resistance of the alloys further, the samples were subjected to potentiodynamic polarization. The experimental polarization curves are presented in **Fig. 5**. The results of Tafel extrapolation are collected in **Table 2**.

The polarization curves of the alloys show a similar behavior for potentials between -1000 and -200 mV (Ag/AgCl). The alloys corrosion is observed at potentials close to -830 mV(Ag/AgCl, **Table 2**). The corrosion is followed by passivation at potentials between -800 and -500 mV(Ag/AgCl) where the potential-current density curves are characterized by stabilization of current density (**Fig. 5**). The passive region of the alloys disappears at breakdown potential (E_{bd}) - see **Table 2**, where a sharp increase of anodic current density is observed. This sharp current density increase is indicative of the breakdown of the passive film [10-13]. On further scanning in the anodic direction the current density eventually peaks to a maximum. This maximum is

known as the critical current density, i_{crit} (Table 2). On further scanning in the anodic direction the current density is seen to slowly decrease (Fig. 5). At a certain point in the far-anodic region the current density eventually becomes independent of the potential. This current density value is referred to as the pseudo-passivation current density, i_p since it is indicative of the pseudo-passivation processes attributable to a formation of a corrosion product films [9-13].

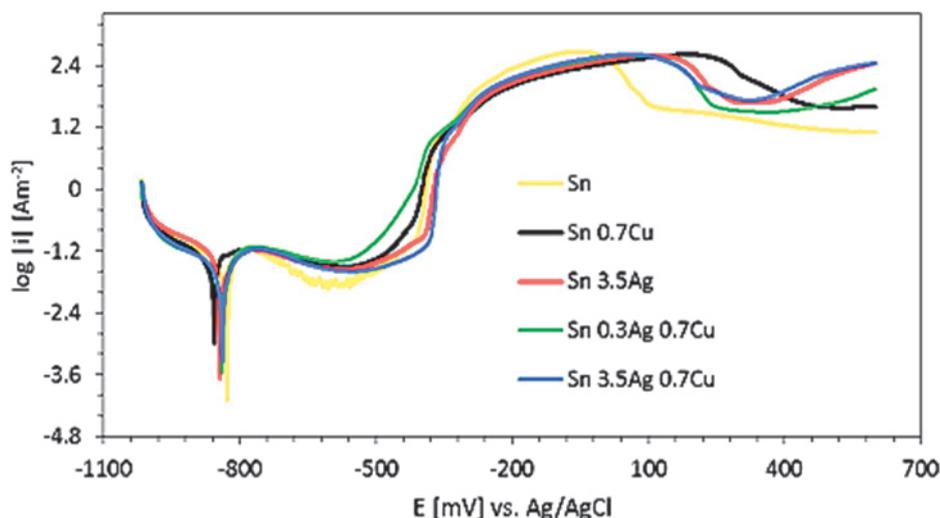


Fig. 5 Potentiodynamic polarization curves of lead-free solders in 3.5 wt.% NaCl solution

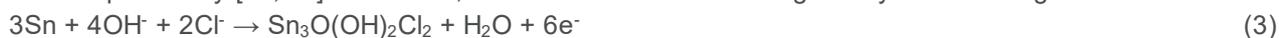
Table 2 Summary of corrosion parameters of lead-free solders with scanning rate at 2 mV/s

Alloys	E_{corr} (mV)	E_{bd} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	i_{crit} (mA/cm^2)	i_p (mA/cm^2)
Sn	-828	-413	1.38	45.71	1.29
Sn-0.7Cu	-856	-486	0.79	40.74	3.89
Sn-3.5Ag	-843	-408	0.80	39.81	4.79
Sn-0.3Ag-0.7Cu	-840	-570	0.83	39.81	3.16
Sn-3.5Ag-0.7Cu	-837	-397	1.03	41.69	5.25

E_{corr} - corrosion potential, i_{corr} - corrosion current density, i_{crit} - critical passivation density, i_p - passivation current density, E_{bd} - breakdown potential

After corrosion, the sample surfaces were subjected to investigation by confocal laser scanning microscopy. The surface topographies are presented in Fig. 6. The intermetallic particles were found as isolated islands in the corroded sample landscape (Fig. 6b, c). The β -Sn grains were preferentially dissolved. It can be suggested that, in the course of the alloys corrosion, the intermetallic particles (Ag_3Sn and Cu_6Sn_5) served as artificial cathodes promoting the tin dissolution.

The anodic reaction is the tin dissolution. Our XRD results of the samples after corrosion experiments indicate that the oxidation product was tin oxyhydroxychloride. This corrosion product has also been observed by other authors previously [12, 14]. Therefore, the anodic reaction can be given by the following scheme



The cathodic reaction is oxygen reduction [14]



The overall corrosion reaction can be given by the following scheme



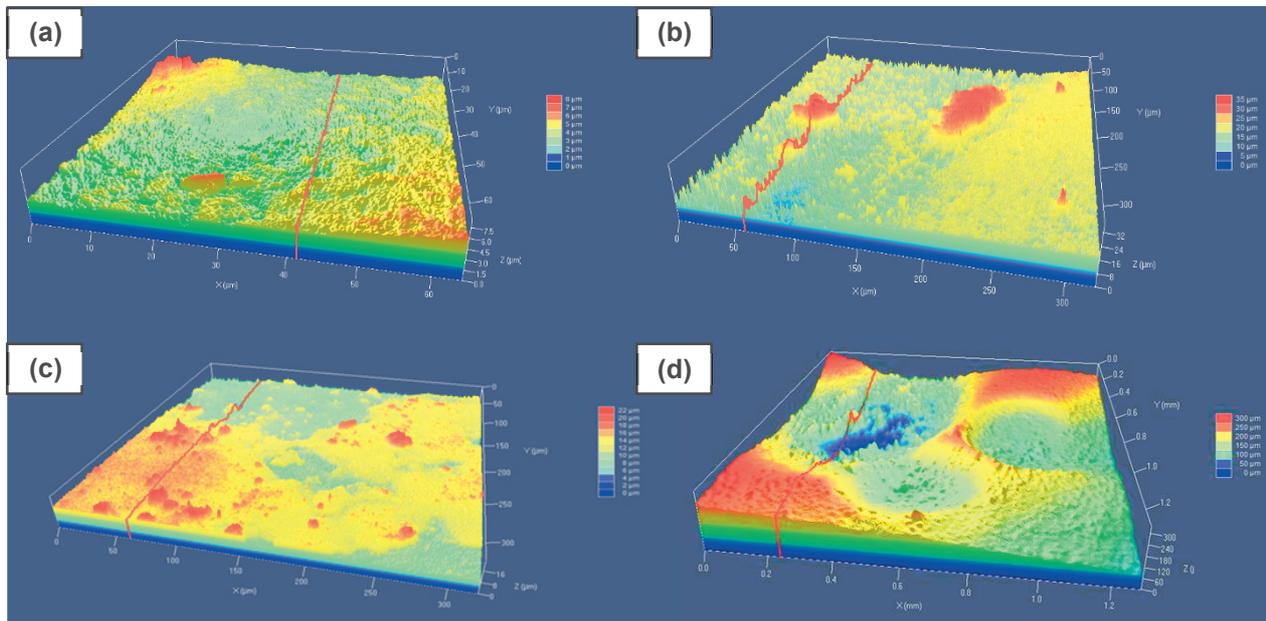


Fig. 6 Microstructures of lead-free solder alloys after corrosion test: a) Sn0.7Cu b) Sn3.5Ag c) Sn3.5Ag0.7Cu d) Sn0.3Ag0.7Cu.

4. CONCLUSION

In the present work, the microstructure and corrosion behavior of four near-eutectic tin-based alloys were investigated. Sn-0.7Cu, Sn-3.5Ag, Sn-0.3Ag-0.7Cu and Sn-3.5Ag-0.7Cu (composition in wt.%) alloys were prepared by induction melting from high purity Sn, Ag and Cu lumps. Each alloy was heterogeneous. The microstructure of the Sn-0.7Cu alloy was found to be composed of β -Sn and a binary eutectic. The microstructure of the Sn-3.5Ag alloy was composed of β -Sn and a eutectic. The microstructures of ternary Sn-0.3Ag-0.7Cu and Sn-3.5Ag-0.7Cu alloys consisted of β -Sn and a ternary eutectic. The binary eutectic of the Sn-0.7Cu alloy was composed of Cu_6Sn_5 and β -Sn phases. The binary eutectic of the Sn-3.5Ag alloy consisted of Ag_3Sn and β -Sn. The ternary eutectic of the Sn-0.3Ag-0.7Cu and Sn-3.5Ag-0.7Cu alloys were composed of β -Sn and Cu_6Sn_5 and Ag_3Sn intermetallic phases.

The corrosion resistance of the alloys was studied by potentiodynamic polarization. Corrosion currents and corrosion potentials were obtained by Tafel extrapolation of the experimental polarization curves. The lowest corrosion currents were found for the Sn-3.5Ag and Sn-0.7Cu alloys.

After corrosion, the sample surfaces were investigated by confocal laser scanning microscopy. The intermetallic particles were found as isolated islands on the corroded sample surface. In the course of alloys corrosion, the intermetallic particles (Ag_3Sn and Cu_6Sn_5) probably served as artificial cathodes promoting the tin dissolution.

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