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Electrochemical Properties of Joints Formed Between Sn-9Zn-1.5Ag-1Bi Alloys and Cu Substrates in a 3.5 wt.% NaCl Solution

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The electrochemical properties of the joints formed between Sn-9Zn-1.5Ag-1Bi alloys and Cu substrates in a 3.5 wt.% NaCl solution have been investigated by potentiodynamic polarization, X-ray diffraction, and scanning electron microscopy. For the Sn-9Zn-1.5Ag-1Bi/Cu joints in a 3.5 wt.% NaCl solution, corrosion current (I_{corr}), corrosion potential (E_{corr}) and corrosion resistance (R_p) are 2.46×10^{-6} A/cm^2, –1.18 V, and 7.54×10^3 Ωcm^2, respectively. Cu_6Sn_5, Cu_5Zn_8, and Ag_3Sn are formed at the interface between the Sn-9Zn-1.5Ag-xBi solder alloy and Cu substrate. The corrosion products of $ZnCl_2$, $SnCl_2$ and ZnO are formed at the Sn-9Zn-1.5Ag-xBi/Cu joints after polarization in a 3.5 wt.% NaCl solution. Pits are also formed on the surface of the solder alloys.

Key words: Solder alloy, electrochemical properties, potentiodynamic polarization, corrosion products, ZnO

INTRODUCTION

Responding to the urgent need for green electronic products, lead-free solders have emerged as substitutes for traditional Pb-Sn solder alloys as major interconnecting materials in electronic packaging processes.[1] For a long time, eutectic 63Sn-37Pb solder has been used as a standard material for joints of electronic components because of its suitable physical properties and low cost. However, lead must be totally phased out from industrial products in the coming years.[2] Among alternative lead-free solders, the Sn-Zn solder system seems to be the most favorable candidate. However, the mechanical behavior of an Sn-9Zn solder alloy is currently not well understood, and in practice its inferior wettability and corrosion resistance remain to be overcome.[3] Takemoto and Funaki[4] have pointed out that adding Ag to an Sn-9Zn lead-free solder alloy inhibits the anodic dissolution of Zn and enhances the wettability of solder on the Cu substrate.

An Sn-9Zn-1.5Ag lead-free solder is a promising material to substitute for Pb-Sn solder alloys, as it significantly improves the shortcomings of an Sn-9Zn solder alloy. Kirkendall voids induced by the different diffusion coefficients of Zn and Cu are often observed at the solder joint between the Sn-9Zn solder alloy and Cu substrate.[5] Chang et al.[6] have reported that the formation of Kirkendall voids at the Sn-9Zn/Cu interface can be inhibited by Ag additions.

Moreover, melting temperature is the most important consideration for the development of solder alloys. A higher reflow temperature in the electronic packaging process causes thermal damage to substrates. In our previous study,[7] the addition of Bi to the Sn-9Zn-1.5Ag solder alloy was beneficial to address the issues of high melting point

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and wettability of this solder alloy on the Cu substrate. A 0.5 wt.% Bi addition to the Sn-9Zn-1.5Ag solder alloy decreases the melting point of the solder alloy and enhances its adhesion strength on the Cu substrate.[7] An Sn-9Zn-1.5Ag-0.5Bi near-eutectic solder alloy has a melting point of 195.9°C and a melting range of 10°C, while the melting point of an Sn-37Pb solder alloy is 183°C.

Corrosion resistance is another issue for lead-free solder alloys. Corrosion products are easily formed and increase current transport resistance in practice. Lower corrosion resistance is representative of a lower current conductive effect and reduces the lifetime of devices. Chang et al.[8] reported the electrochemical behavior of Sn-9Zn-xAg lead-free solders in a 3.5 wt.% NaCl solution. However, the electrochemical parameters and corrosion products of Sn-9Zn-1.5Ag-1Bi/Cu joints in a 3.5 wt.% NaCl solution have not yet been discussed in detail.

The electrochemical properties of the Sn-9Zn-1.5Ag-1Bi/Cu joints have been studied by polarization, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The objectives of this study were (1) to compare the corrosion characteristics of Sn-9Zn-1.5Ag and Sn-9Zn-1.5Ag-1Bi solder alloys, and (2) to identify the corrosion products of Sn-9Zn-1.5Ag-1Bi solder alloys in a 3.5 wt.% NaCl solution.

EXPERIMENTAL PROCEDURE

Sample Preparation

The Sn-9Zn-1.5Ag and Sn-9Zn-1.5Ag-1Bi solder alloys (in wt.%) were prepared by melting pure Sn, Zn, Ag, and Bi (purity 99.9%). The oxide on each pure metal was removed with a 5 vol.% HCl solution at ambient temperature and degreased with a 5 wt.% NaOH solution at 70°C. For the Sn-9Zn-1.5Ag solder alloy, pure Sn, Zn, and Ag were melted at 600°C in a stainless-steel crucible and stirred to homogenize the mixture. To avoid the interaction between the stainless-steel crucible and molten solder alloys at 600°C, especially those containing Zn, the molten solder alloy was stirred to homogenize and cooled in air to 250°C before dipping the Cu substrate. Finally, the solder alloy was cast in a metal mold at 250°C with a diameter of 3 cm and cooled in air.

For the Sn-9Zn-1.5Ag-1Bi solder alloy, pure Sn, Zn, and Ag were also melted at 600°C in a stainless-steel crucible and stirred to homogenize the mixture. When the melted alloy was cooled to 300°C and the dross was removed, pure Bi was added to the melted alloy and stirred to homogenize the metals the mixture. An oxygen-free, high-conductivity Cu plate with dimensions of 70 mm × 25 mm × 2 mm was used as a substrate and cleaned with the same procedure as described above. After pretreatment, a Cu substrate was fluxed in a 3.5 wt.% DMAHCl solution (3.5 wt.% dimethylammonium chloride dissolved in ethanol) for 10 s to enhance activity and avoid reoxidizing the surface. Subsequently, Cu substrates were immersed in molten Sn-9Zn-1.5Ag and Sn-9Zn-1.5Ag-1Bi at 250°C for 60 s at a dipping rate of 11.8 mm/s to obtain a flat surface. The details are described in our previous study.[7]

Sample Characterization

The electrochemical test was conducted according to the Japanese International Standard (JIS G 0579). A potentiostat (model 273, EG&G, USA) was utilized to determine the overpotential of the solder alloys. A 3.5 wt.% NaCl solution (Wako Pure Chemical Industries. Ltd., 99.5% purity, Osaka, Japan) was used as a corrosion medium and purified N_2 as an ambient gas, as shown in Fig. 1.

A saturated calomel electrode (SCE) with a stable potential of 0.244 V in a saturated KCl solution was used as a reference electrode. A Pt-coated Ti net was used as a counter electrode. The sample was cathodically treated at $-1.5\ V_{SCE}$ for 10 min and potentiodynamic polarization was conducted from -1.7 to $0.5\ V_{SCE}$ at 1 mV/s. Before the electrochemical test, the sample was ground with sandpapers to expose a fresh surface. After the potentiodynamic polarization test, the corrosion products on the sample surface were cleaned with acetone and determined by XRD (D-MAX III β, Rigaku, Tokyo) at a scanning rate of 2°/min for 2θ from 20° to 80°. The microstructure was observed with a scanning electron microscope (M-SEM, JXA-840, JEOL, Tokyo).

RESULTS AND DISCUSSION

Electrochemical Properties of Sn-9Zn-1.5Ag-xBi/Cu Joints

The polarization curves of the Sn-9Zn-1.5Ag-xBi/Cu joints in a 3.5 wt.% NaCl solution are shown in Fig. 2. The corrosion potentials (E_{corr}) are -1.21 V

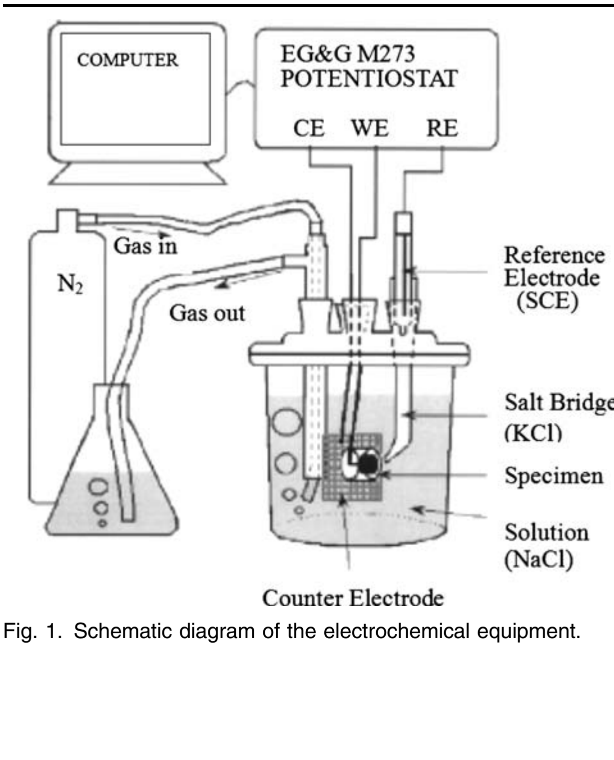

Fig. 1. Schematic diagram of the electrochemical equipment.

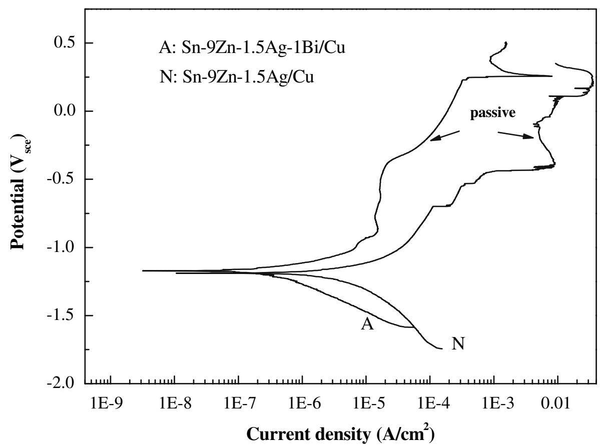

Fig. 2. Polarization curves for Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints in a 3.5 wt.% NaCl solution.

and −1.18 V for Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints, respectively. The corrosion potentials of the Sn-9Zn-1.5Ag-xBi/Cu joints in a 3.5 wt.% NaCl solutions are listed in Table I. These indicates that the E_{corr} value of the Sn-9Zn-1.5Ag-1Bi/Cu joints (−1.18 V) is higher than that of the Sn-9Zn-1.5Ag/Cu joints (−1.21 V) in a 3.5 wt.% NaCl solution. Therefore, the Sn-9Zn-1.5Ag-1Bi solder alloy has better corrosion resistance than that of the Sn-9Zn-1.5Ag solder alloy with Cu as a substrate.

Moreover, Fig. 2 also indicates that the I_{corr} value of the Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints are 2.65×10^{-6} and 2.46×10^{-6} A/cm^2, respectively. Low I_{corr} represents corrosion resistance,[8] and this result indicates that 1 wt.% Bi addition to the Sn-9Zn-1.5Ag solder alloy decreases the corrosion current density.

The β_a and β_c values are obtained from the anodic and cathodic Tafel slopes, as shown in Table I, implying that, the higher the Tafel slope, the lower the corrosion rate.[9,10] In this study, the β_a values for the Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints are 62.3 and 64.7 mV/dec, and the β_c values are 121.1 and 125.6 mV/dec, respectively. This result also indicates that 1 wt.% Bi addition to the Sn-9Zn-1.5Ag alloy enhances corrosion resistance, and Bi addition to the Sn-9Zn-1.5Ag solder alloy also lowers the melting temperature and improves the wettability of solders.[7] This phenomenon is due to the fact that Bi inhibits the overall metal dissolution rate, causing a large anodic Tafel slope. In fact, Bi addition to a Sn-9Zn solder also slightly increases the corrosion resistance in a salt solution.[11,12]

As shown in Fig. 2, the Sn-9Zn-1.5Ag/Cu joints have a passive range from 10^{-3} to 10^{-2} A/cm^2. However, the passive range for the Sn-9Zn-1.5Ag-1Bi/Cu joints is from 10^{-5} to 10^{-3} A/cm^2. The lower current density of the passive range indicates that a steady current density is more likely to occur during the electrochemical test. Therefore, the current density of the Sn-9Zn-1.5Ag-1Bi/Cu joints is lower than that of Sn-9Zn-1.5Ag/Cu in the passive range. Moreover, Table I also shows that the corrosion resistances are 6.74×10^3 and 7.54×10^3 Ωcm^2 for the Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints, respectively. Therefore, 1 wt.% Bi addition to an Sn-9Zn-1.5Ag solder alloy leads to higher corrosion resistance.

Corrosion Products of the Sn-9Zn-1.5Ag-*x*Bi/Cu Joints

Figure 3 shows the XRD patterns of the Sn-9Zn-1.5Ag-xBi/Cu joints for the Cu substrate dipped in molten solder at 250°C for 60 s. It indicates that Cu_6Sn_5, Cu_5Zn_8, and Ag_3Sn have formed at the Sn-9Zn-1.5Ag-xBi solder alloy/Cu interface. Chang et al.[13] also demonstrated that Ag occupies the interstitial sites and reacts with Sn to form Ag_3Sn, and Ag_3Sn is formed at the Sn-9Zn-xAg solder alloy/Cu interface when the Ag content in the solder alloy

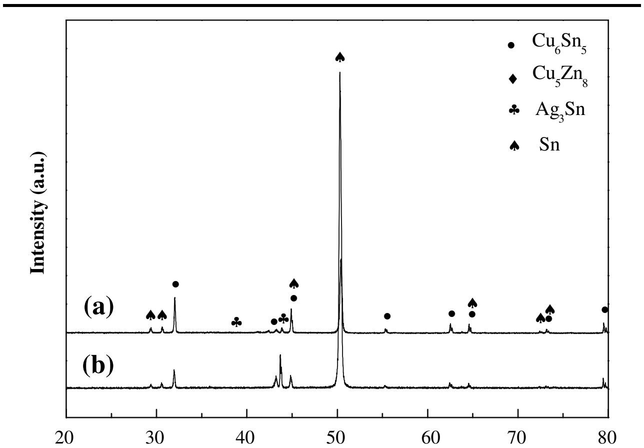

Fig. 3. XRD patterns for as-soldered: (a) Sn-9Zn-1.5Ag/Cu and (b) Sn-9Zn-1.5Ag-1Bi/Cu joints for the Cu substrate dipped in molten solder at 250°C for 60 s.

Table I. Electrochemical Properties of Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu Interfaces in a 3.5 wt.% NaCl Solution

Characteristics	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (V)	I_{corr} (A/cm^2)	R_p (Ωcm^2)
Solder alloys					
Sn-9Zn-1.5Ag/Cu	62.3	121.1	−1.21	2.65×10^{-6}	6.74×10^3
Sn-9Zn-1.5Ag-1Bi/Cu	64.7	125.6	−1.18	2.46×10^{-6}	7.54×10^3

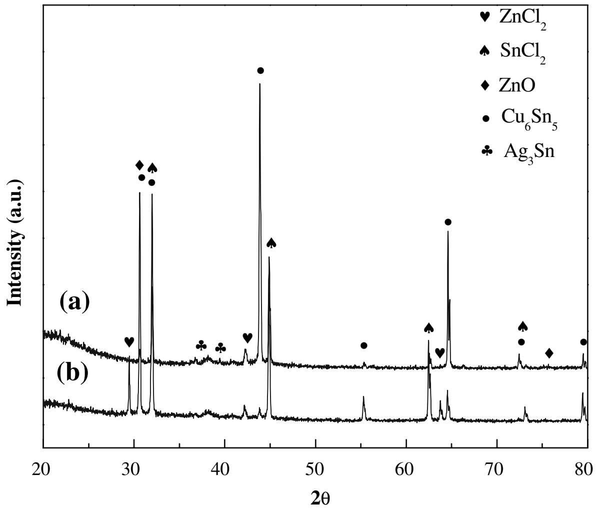

Fig. 4. XRD patterns of: (a) Sn-9Zn-1.5Ag/Cu and (b) Sn-9Zn-1.5Ag-1Bi/Cu joints after polarization in a 3.5 wt.% NaCl solution.

is above 0.1 wt.% because the solubility of Ag in Sn is quite low even at the eutectic temperature. Moreover, Ahat et al.[14] demonstrated the formation of Ag_3Sn in an Sn-3.5Ag solder alloy. In addition, the base-centered cubic (bcc) γ-Cu_5Zn_8 layer is one of the intermetallic compounds (IMC) layers formed at the Sn-9Zn/Cu and Sn-Zn-Al/Cu interfaces, as reported by Yu et al.[15]

Figure 4 shows the XRD patterns of the Sn-9Zn-1.5Ag-*x*Bi/Cu interfaces after dynamic polarization in a 3.5 wt.% NaCl solution. It indicates that the phases of Cu_6Sn_5, Ag_3Sn, $ZnCl_2$, $SnCl_2$, and ZnO are formed at the Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints. However, Cu_6Sn_5 and Ag_3Sn are formed after the Cu substrate has been dipped in the solder alloy at 250°C for 60 s. Cu_6Sn_5 and Ag_3Sn are more noble than an Sn matrix, and therefore do not dissolve in a 3.5 wt.% NaCl solution when acting as a cathode.[8] In addition, Cl^- ions in a 3.5 wt.% NaCl solution react with Zn component in the solder to form $ZnCl_2$.

Moreover, Zn is active to react with O_2, forming a ZnO layer along the grain boundaries, which have a smaller area but higher oxidation potential than the bulk.[16–18] $SnCl_2$ is another corrosion product for the Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints. On the other hand, Sn is an anode in electrochemical reactions and reacts with Cl^- to form $SnCl_2$, which is quite soluble in an aqueous solution and has also been observed in the Sn-Zn-Al solder alloy.[18]

Micrographs of the Sn-9Zn-1.5Ag-*x*Bi/Cu Interfaces before and after the Electrochemical Test

The micrographs of the as-soldered Sn-9Zn-1.5Ag-*x*Bi/Cu interface are shown in Fig. 5a and c. Cu_6Sn_5 and Cu_5Zn_8 IMCs are formed at the interface of the solder alloy and the Cu substrate. The Cu diffuses to the solder and reacts with Sn to form Cu_6Sn_5, and Zn diffuses to the Cu to form the Cu_5Zn_8. These two IMCs affect the adhesion strength and wettability of the solder on the Cu substrate.[19] In addition, a planar Ag_3Sn also forms in the Sn matrix. Chang et al.[13] have shown that fine Ag_3Sn particles form at the Sn-9Zn-0.5Ag/Cu interface. Moreover, Fig. 5a and c also show that Cu_6Sn_5 and Cu_5Zn_8 are scallop

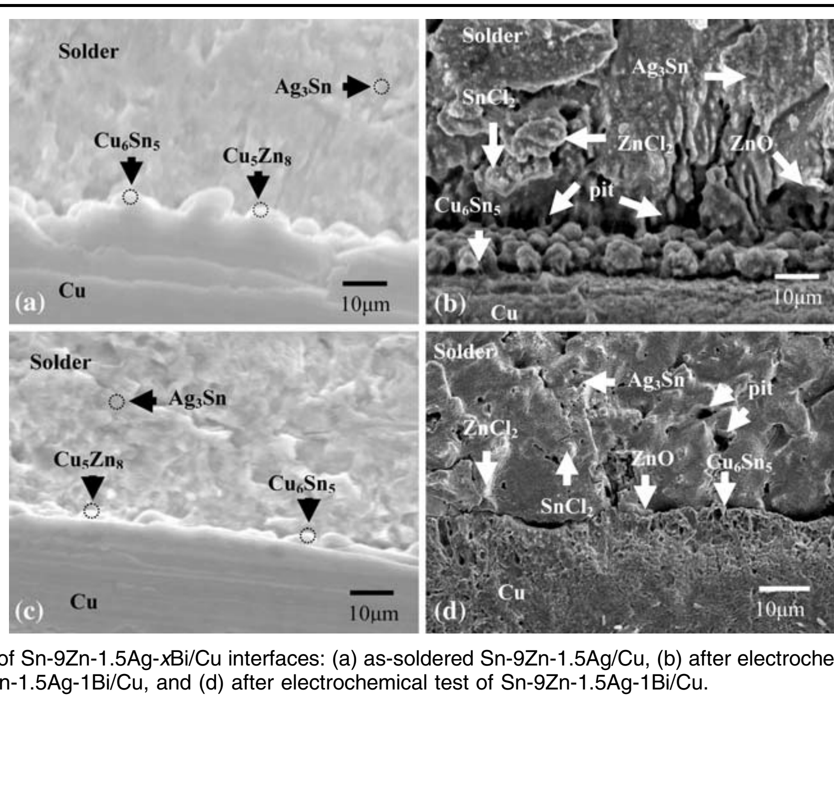

Fig. 5. SEM micrographs of Sn-9Zn-1.5Ag-*x*Bi/Cu interfaces: (a) as-soldered Sn-9Zn-1.5Ag/Cu, (b) after electrochemical test of Sn-9Zn-1.5Ag/Cu, (c) as-soldered Sn-9Zn-1.5Ag-1Bi/Cu, and (d) after electrochemical test of Sn-9Zn-1.5Ag-1Bi/Cu.

shaped in the interface of the solder/Cu as-soldered at 250°C for 60 s. It is concluded that Bi addition to Sn-9Zn-1.5Ag solder alloy does not affect IMC formation.

Figure 5b and d are the micrographs of the as-corroded Sn-9Zn-1.5Ag-*x*Bi/Cu interface after the electrochemical test in a 3.5 wt.% NaCl solution. Small pits are found at the Sn-9Zn-1.5Ag-*x*Bi solder alloy/Cu interface. In addition, the corrosion products of ZnO, $ZnCl_2$, and $SnCl_2$ are also found, agreeing with the XRD results shown in Fig. 4. O_2 gas from the electrolysis of H_2O is trapped in the pits and reacts with Zn^{2+} to form ZnO. Due to the Cl^- ions being aggressively adsorbed on the facility films, $ZnCl_2$ and $SnCl_2$ corrosion products are formed at the Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu interfaces in a 3.5 wt.% NaCl solution.[17,20]

In addition, Fig. 5b and d also show some pits formed at the solder alloy/Cu interface because: (1) Cl^- ions in a 3.5 wt.% NaCl solution attacks both the solder alloy and Cu substrate, and (2) ZnO and $SnCl_2$ corrosion products act as cathodes and Sn as an anode, causing the formation of pits.[21,22] Figure 5b and d reveal that Sn-9Zn-1.5Ag/Cu and Sn-9Zn-1.5Ag-1Bi/Cu joints have the same corrosion products of ZnO, $ZnCl_2$ and $SnCl_2$ after electrochemical tests; however, the pit size of the Sn-9Zn-1.5Ag-1Bi/Cu joints is smaller than that of the Sn-9Zn-1.5Ag/Cu joints. The reason is that the corrosion resistance of the Sn-9Zn-1.5Ag-1Bi/Cu joints is higher than that of the Sn-9Zn-1.5Ag/Cu joints in a 3.5 wt.% NaCl solution. In addition, Chang et al.[17] demonstrated that the pit formation is due to the dissolution of $AgZn_3$ and Ag_5Zn_8 for the Sn-9Zn-1.5Ag/Cu joints during an electrochemical test. However, in the present study, $AgZn_3$ and Ag_5Zn_8 are not found at the Sn-9Zn-1.5Ag/Cu interface; hence, it is suggested that the pit formation in the present study may be ascribed to the dissolution of Cu_5Zn_8.

CONCLUSIONS

The electrochemical properties of the joints formed between Sn-9Zn-1.5Ag-1Bi alloys and Cu substrates in a 3.5 wt.% NaCl solution have been investigated by polarization, XRD, and SEM. The corrosion resistance (R_p), current density (I_{corr}) and corrosion potential (E_{corr}) are found to be $6.74 \times 10^3\ \Omega cm^2$, 2.65×10^{-6} A/cm^2, and −1.21 V for Sn-9Zn-1.5Ag/Cu joints and $7.54 \times 10^3\ \Omega cm^2$, 2.46×10^{-6} A/cm^2, and −1.18 V for Sn-9Zn-1.5Ag-1Bi/Cu joints, respectively. $SnCl_2$ is easily attacked by Cl^- ions, but ZnO is the most stable product in the Zn^{2+}/H_2O system. The passive range causes continuous oxidation and protects substrates and solders. Sn-9Zn-1.5Ag-1Bi/Cu joints have a passive range from 10^{-5} to 10^{-3} A/cm^2. Scallop-shaped Cu_5Zn_8 and Cu_6Sn_5 and planar Ag_3Sn IMCs form at the interface of as-soldered Sn-9Zn-1.5Ag-*x*Bi/Cu. Corrosion products of $SnCl_2$, $ZnCl_2$, ZnO, and pits are formed at both solder/substrate interfaces, and the pit size at the Sn-9Zn-1.5Ag-1Bi/Cu interfaces is smaller than that at the Sn-9Zn-1.5Ag/Cu interface.

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