Contents lists available at ScienceDirect

Corrosion Science

Electrochemical behavior of a lead-free Sn–Cu solder alloy in NaCl solution

Wislei R. Osório [a,b,*], Emmanuelle S. Freitas [b], José E. Spinelli [c], Amauri Garcia [b]

[a] School of Applied Sciences/FCA, University of Campinas, UNICAMP, P.O. Box 1068, 1300, Pedro Zaccaria St., Jd. Sta Luiza, 13484-350 Limeira, SP, Brazil
[b] Department of Materials Engineering, University of Campinas, UNICAMP, P.O. Box 6122, 13083-970 Campinas, SP, Brazil
[c] Department of Materials Engineering, Federal University of São Carlos – UFSCar, Washington Luis Rd at km 235, 13565-905 São Carlos, SP, Brazil

ARTICLE INFO

ABSTRACT

Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization techniques and an equivalent circuit analysis are used to evaluate the electrochemical corrosion behavior of Sn–Cu alloy samples in a naturally aerated 0.5 M NaCl solution at 25 °C. It has been found that a better electrochemical corrosion resistance is provided by a coarser cellular microstructure array. It has also been found that the corrosion current density (i_{corr}) is of about a quarter when compared with that of the finest microstructure examined. Such behavior is attributed to both localized strains between the Sn-rich phase and intermetallic (IMC) particles and the cathode/anode area ratios. The effect of copper alloying on i_{corr} is also discussed.

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1. Introduction

Lead-containing solder alloys have been banned from electronic and microelectronic products by the environmental protection agencies (RoHS and WEEE) [1–3]. With the legislation prohibiting or restricting the use of the traditional Sn–Pb solder alloys [1–5], alternative successor solder alloys are impressively required. A number of lead-free solders have been studied as potential Pb-free alternatives to replace Sn–Pb alloys, e.g. Sn–Ag, Sn–Zn, Sn–Bi, Sn–Cu, and various ternary and quaternary alloys combining these aforementioned elements. However, these alloys have also to meet technical and operational requirements, such as appropriate melting point, wettability, thermal and electrical conductivity, mechanical and creep strengths, corrosion resistance and low cost [1–5]. In this sense, Sn–Cu alloys emerge as promising solders for electronic applications due to their inherent low cost and good comprehensive properties [6].

Distinct microstructural arrays can be formed during soldering, which are intimately associated with the corresponding cooling rate. It is well known that the resulting microstructure, unsoundness, strength, and corrosion behavior of solders depend on the thermal processing variables imposed during soldering or thermal cycling [3–12].

A number of investigations in the literature focused on correlations between microstructure and the corresponding properties for a number of solder alloys [5–13]. However, there is a lack of studies enlightening the dependence of the scale of microstructural parameters of a eutectic Sn–0.7 wt.% Cu solder alloy on the electrochemical corrosion behavior. Good corrosion behavior is demanded from a solder alloy, either during soldering of a chip assembly into a PCB (printed circuit board) or when the solder joints are directly exposed to aggressive media or air pollutant moistures in an industrial environment [6–8,14].

Some investigations [3,7,14] developed comparative analyses of the corrosion behavior of Sn–Cu alloys and other Pb-free solders. However, the effects of the microstructural array on the electrochemical behavior have not been considered.

Gao et al. [7] have recently reported results of a potentiodynamic polarization study on a Sn–0.75 wt.% Cu alloy in an oxygen 3.5% NaCl solution. In this study, the corroded product has been systematically characterized, which has permitted a complete discussion concerning the active dissolution of the Sn-rich matrix, passivation on the surface of the examined samples and pitting formation.

In a recent study with a Sn–2.8 wt.% Cu solder alloy [15], it was found that a cooling rate about 15 °C/s induces fine and homogeneously distributed primary Cu_3Sn and Cu_5Sn_6 IMCs particles embedded in a continuous Sn-rich matrix. This microstructural array has provided a corrosion current density of about 2 times

higher than that of a coarser microstructure array, which had been formed under a cooling rate of about 1.2 °C/s. It has also been recently reported [16] a comparison between the electrochemical behavior of Sn–2 wt.% Ag and Sn–2.8 wt.% Cu alloys samples, having microstructures formed under cooling rates of about 10 and 15 °C/s. It was found that the Sn–2 wt.% Ag alloy has evidenced a corrosion current density in a sodium chloride solution at room temperature of about 4 times lower than that presented by the Sn–2.8 wt.% Cu alloy. However, the great disadvantage of the Sn–2 wt.% Ag alloys is its relative cost of about 1.5 times higher than that of the Sn–2.8 wt.% Cu alloy [16].

Despite the mentioned studies on Sn–Cu solder alloys, correlations between impedance parameters, potentiodynamic polarization and quantitative and qualitative features of the resulting microstructure array are still scarce in the literature. This can be useful for manufacturers with a view to designing solders microstructures as a function of desired corrosion properties.

The present experimental investigation focuses on the effect of the scale of the resulting microstructure array, constituted by a eutectic mixture (Sn-rich phase + Cu_6Sn_5 IMC particles) embedded in an Sn-matrix, on the resulting electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization plots of a eutectic Sn–0.7 wt.% Cu solder alloy, with tests performed into a naturally stagnant 0.5 M NaCl (3.5% NaCl) solution at room temperature.

2. Experimental procedure

2.1. Specimens preparation

Sn–0.7 wt.% Cu alloy samples were prepared using commercially pure (c.p.) Sn (99.993 wt.%) and Cu (99.991 wt.%). Areas of 100 mm² from 3 different specimens were taken for the analyses. The main impurities were determined by Energy Dispersive X-ray Spectroscopy (EDS) coupled with SEM, and confirmed through an X-ray fluorescence technique. The detected impurities are: Fe (0.001 wt.%), Si (0.0018 wt.%), Zn (0.004 wt.%), and Pb (0.0016 wt.% and Fe (0.007 wt.%), respectively, besides other elements found with concentrations less than 100 ppm.

A water-cooled transient solidification set-up was used to obtain directionally solidified Sn–Cu alloy samples, in which heat is extracted only through the water-cooled bottom promoting vertical upward directional solidification. More details of this solidification assembly can be found in previous articles [4,8,15]. Three selected specimens were extracted from longitudinal sections of the vertically solidified casting at positions 06, 46 and 85 mm from the bottom of the casting: named P1, P2 and P3, respectively. The Cu concentration at these positions was shown to be: 0.72 (±0.02) wt.%, 0.69 (±0.01) wt.% and 0.68 (±0.01) wt.%, respectively. These positions were chosen in order to allow the effect of a range of resulting microstructural parameters on the corrosion behavior to be investigated.

The Sn–0.7 wt.% Cu alloy casting was sectioned along the longitudinal direction and a solution of 2 mL HCl, 10 g $FeCl_3$ and 100 mL H_2O was used to reveal the macrostructure, as shown in Fig. 1. In order to reveal the microstructures, the samples were ground and etched with a solution of 92% (vol.) CH_3OH, 5% (vol.) HNO_3 and 3% (vol.) HCl during about 5 s.

Microstructural characterization was performed using both a Field Emission Gun (FEG) – Scanning Electron Microscope (SEM), Philips (XL30 FEG) coupled to an Energy Dispersive Spectroscopy – EDS (Oxford Link ISIS 300) and an optical image processing system Olympus, GX51 (Olympus Co., Japan). The primary dendritic arm spacing (λ_1) and the cellular spacing (λ_c) were measured using the triangle method, as previously described by Gunduz and Çardili [17].

2.2. Preparation of corrosion tests

The Sn–Cu alloy samples for corrosion tests were extracted from the positions in the casting shown in Fig. 1. These selected samples were positioned into a corrosion cell with a circular 1.0 (±0.02) cm² surface immersed in a naturally aerated and stagnant 500 mL of a 0.5 M NaCl solution at 25 °C, with a pH of 7.15 (±0.5).

The samples were ground to a 1200 grit surface finish using silicon carbide paper, followed by distilled water washing and air drying before electrochemical measurements. The samples after ground were immediately positioned in the cell kit and the electrolyte was poured into the cell. This procedure was adopted for all samples examined. It is important to remark that duplicate tests for both EIS and potentiodynamic polarization curves were carried out.

EIS measurements began after an initial delay of about 20 min in order to standardize all the experiments. This period of time was considered enough for stabilization of the potential since the EIS tests were carried out under open-circuit potential and an unsteady-state condition could provide distortions on measurements. A potentiostat coupled to a frequency analyzer system, a glass corrosion cell kit with a platinum counter-electrode and a saturated calomel reference electrode (SCE) were used to perform the EIS tests. The potential amplitude was set to 10 mV (SCE) at peak-to-peak (AC signal) in open-circuit, with 5 points per decade and the frequency range was set from 100 mHz to 100 kHz.

Immediately after the EIS measurements, the polarization tests were also carried out at the same positions in a 0.5 M NaCl solution at 25 °C. These tests were conducted by stepping the potential at open-circuit with a scan rate of 0.1667 mV s^{-1} from −900 mV (SCE) to −350 mV (SCE). Using an automatic data acquisition system, the potentiodynamic polarization curves were plotted and the corrosion current density, passivation potential and corrosion potential were estimated. A selected model (ZView® version 2.1b) for equivalent circuit quantification has also been used.

3. Results and discussion

3.1. Macro and microstructure arrays

The revealed macrostructure along the longitudinal direction of the Sn–Cu alloy casting is shown in Fig. 1. Typical microstructure arrays are also shown in Figs. 1 and 2 at distances P1 = 06 mm, P2 = 46 mm and P3 = 85 mm from the cooled surface of the casting. Fig. 2 shows the primary dendritic arm (λ_1) and cellular spacings (λ_c) as a function of position in the casting. The average values of λ_1 and λ_c of the samples at positions P1 and P2 and P3 are 25 (±5) μm, 75 (±10) μm and 105 (±12) μm, respectively. From these micrographs, it can be clearly seen that for regions closer to the casting surface (cooled bottom) up to a position (P) of about 15 mm, the as-cast microstructure is characterized by a well-defined dendritic array. In this region, the cooling rate is the highest (at position 06 mm the cooling rate it was about 2.5 °C/s) decreasing towards the top of the casting (e.g. at P2 and P3 the cooling rates were 0.6 °C/s and 0.35 °C/s, respectively). On the other hand, a cellular array prevails from positions P2 and P3, as shown in Figs. 1 and 2. It can be seen that three distinct microstructural patterns are characterized: (i) dendritic, (ii) dendrite-to-cellular transition, and (iii) cellular arrays. It can be observed that a dendritic-to-cellular transition occurred as a function of the imposed solidification thermal parameters. A detailed discussion concerning the role of solidification thermal parameters on the morphological microstructural transition from cells to dendrites can be found in previous studies [18–20].