Evidence for Ag participating the electrochemical migration of 96.5Sn-3Ag-0.5Cu alloy

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Abstract:

Ag participating the electrochemical migration (ECM) of Sn-Ag based alloys is still controversial. In this work, Ag^+ concentration in electrolyte layer and Ag distribution in dendrites formed during the ECM of 96.5Sn-3Ag-0.5Cu alloy were investigated using Inductively Coupled Plasma Source Mass Spectrometer and Scanning Transmission Electron Microscopy, respectively. The results show that Ag^+ can be detected in electrolyte layer when the anodic polarization potential applied on the 96.5Sn-3Ag-0.5Cu alloy is high enough. Under such a condition, Ag could also be found in dendrites. Therefore, it can be concluded that Ag participates the ECM of 96.5Sn-3Ag-0.5Cu alloy, but it is potential-dependent.

Keywords:

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1. Introduction

Electrochemical migration (ECM) is an important phenomenon related to the failure of electronics. This process occurs when two oppositely biased and closely spaced electrodes are connected by a continuous electrolyte layer. Metal ions are produced at the anode and then migrate toward the cathode, where they can be reduced to metallic dendrite and grows toward the anode [1,2]. As soon as the dendrite reaches the anode, the short circuit occurs and then causes the failure of electronics. Therefore, ECM significantly compromises the reliability of electronics.

The ECM of Sn-Ag and Sn-Ag-Cu alloys has been studied extensively since they are currently the most widely used solder materials in electronics. However, the studies on Ag participating the ECM of Sn-Ag and Sn-Ag-Cu alloys solder are still controversial. Jung et al. thought that Ag did not take part in the ECM of Sn-3Ag-0.5Cu alloy in NaCl and Na_2SO_4, and they believed that Sn was the only element that contributed to ECM of Sn-3Ag-0.5Cu solder alloy [3]. Similarly, Tanaka et al. also reported that in Sn-3.5Ag solder alloys, Ag combines with Sn to form a stable compound Ag_3Sn that did not dissolve during ECM, and therefore Ag could not be found and the migration resistance of Sn-Ag solder alloys was related to the dissolution characteristics of Sn [4]. Yu et al. also reported that Ag had no migration due to the formation of intermetallic compounds in the Sn-Ag based alloys [5]. However, He et al. reported that Ag could be detected occasionally in the dendrites formed in the ECM of 96.5Sn-3Ag-0.5Cu solder alloy, although Sn always dominated composition of dendrites [6]. Furthermore, Medgyes et al. used Scanning

Transmission Electron Microscopy to detect the composition of dendrites formed in the ECM of 98.9Sn-0.3Ag-0.7Cu alloy and 98.4Sn-0.8Ag-0.7Cu alloy, and Ag could be found in some parts of the dendrites [7]. Therefore, it is still an open question that Ag takes part in the ECM of Sn-Ag and Sn-Ag-Cu alloys or not.

The addition of Ag into Sn matrix could form a chemical stable intermetallic compound Ag_3Sn, in which Ag was thought that it was difficult to escape during the ECM process [8]. This was the principle reason why some researchers thought the Ag did not take part in the ECM of Sn-Ag based alloys [3-5]. However, based on the principle of electrochemistry, it is easily known that the release of Ag from Ag_3Sn strongly depends upon the anodic polarization potential that applied on Ag_3Sn. Namely, once the potential applied on the anode is high enough to cause the dissolution of Ag_3Sn and the generation of Ag^+ during ECM, Ag would take part in the ECM.

According to the definition of ECM, ECM can be considered as a consecutive three-step process: (i) dissolution of metal, (ii) ion migration and (iii) deposition of metal ions [2]. During the ECM of Sn-Ag or Sn-Ag-Cu alloys, as soon as the dissolution of Ag_3Sn occurs and Ag^+ is produced, then it migrates in the electrolyte layer, finally deposited at cathode. Therefore, Ag element could be expected to be found in the electrolyte layer, or in dendrite, or both. However, in the previous work [3-5], most of researchers only tried to detect Ag in dendrites using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM+EDS). In this case, it is easily to conclude inaccurately that Ag does not take part in the ECM if the amount of Ag is not sufficient or the accuracy of the detector is not high enough.

The present work focuses on: (1) to determine whether Ag takes part in the ECM of Sn-Ag based solders or not, and (2) to clarify why Ag takes part in or does not take part in the ECM of such materials. The ECM of 96.5Sn-3Ag-0.5Cu alloy was investigated using thin electrolyte layer method [9] in this work. Ag^+ in the electrolyte was detected using Inductively Coupled Plasma Source Mass Spectrometer (ICP-MS) during the ECM process, and Scanning Transmission Electron Microscopy (STEM) was employed to examine the Ag in the dendrites formed during the ECM.

2. Experimental

2.1 Materials and setup for electrochemical migration test

96.5Sn-3Ag-0.5Cu alloy specimen with the dimensions of 2 × 5 × 10 mm was used in this work. Two identical specimens, i.e. a working electrode (WE) and a counter electrode (CE), were embedded in an epoxy resin cylinder with 0.5 mm distance in parallel direction, as shown in Fig. 1a. A copper wire was welded to the backside of each electrode to ensure electrical contact for electrochemical measurements. On the upper surface of the epoxy resin cylinder, a hole with a diameter of 1 mm was drilled through at the position of 1 mm apart from the working electrode and counter electrode. The hole was filled with porous ceramics as a salt bridge to generate an ionic path which can decrease the solution resistance between WE and reference electrode (RE). The bottom of the epoxy resin cylinder was connected to a U-shape plexiglass tube which was filled with saturated KCl solution (Fig. 1b). A saturated calomel electrode (SCE) as RE was placed into the tube from one end. In the previous work [9-12], a two-electrode system consisting of WE and CE was usually used in the ECM test, trying to simulate the operating condition of electronics. However, the exact potential applied on the working electrode was missing. This setup allows us to control and record the exact potential that applied on WE (WE acted as an anode in this work) during the ECM measurement.

Before each experiment, the electrode (epoxy resin cylinder) surface was ground up to 1200 grit with silicon carbide paper. Subsequently, the surface was rinsed with deionized water, degreased with acetone and dried in cool air. Then the pretreated electrodes were put into a plexiglass chamber where there was a horizontal stage, which could be leveled using a spirit level, as shown in Figs. 1b and c. A certain amount of electrolyte was placed on the electrode surface to form a continuous and smooth electrolyte layer. Thickness of the electrolyte layer was 200 μm in this work. The thickness of the electrolyte layer was measured using a set-up consisting of a sharp Pt needle (Φ=0.05 mm) with a Z-stage equipped with a micrometer (Fig. 1c). The detailed information and method of thickness measurement were described elsewhere [13]. The same electrolyte was also added into the plexiglass chamber to minimize the evaporation. This setup which is similar to those reported in previous work about atmospheric corrosion or ECM makes it possible to perform *in situ* electrochemical migration measurements under thin electrolyte layer [13-15].

2.2 Electrochemical migration test

The electrolyte was 1 mM NaCl solution (pH6.7), which was prepared from deionized water (18.2 MΩ cm in resistivity) and analytical grade reagents. All the potential is with respect to SCE. The open circuit potential of 96.5Sn-3Ag-0.5Cu alloy under 200-μm-thick 1 mM NaCl layer is -0.62 V vs. SCE. Different potential (-0.12 V vs. SCE, 0.38 V vs. SCE and 2.38 vs. SCE) was applied on the working electrode surface to generate a DC bias across the WE and CE. The current and potential were recorded using a CS350 electrochemical test system (Wuhan Corrtest, China). All electrochemical migration measurements were performed at 25 ^{o}C and 90% RH in this work.

2.3 The measurements of ions concentration and dendrites composition

Concentrations of the ions including tin ions, copper ions and silver ions in the electrolyte were detected by the Inductively Coupled Plasma Source Mass Spectrometer (ICP-MS, ELAN DRC-e, PerkinElmer America). The location of taking the electrolyte was at the center of the electrode system shown in Fig.1a. Three parallel samples were tested to guarantee the reproducibility.

To check the composition of dendrites, Scanning Transmission Electron Microscopy (STEM) was used. It is well known that the dendrites formed in the ECM are extremely thin and fragile [7,10], furthermore, the substrate on which dendrites are formed is not conductive. In order to preparation a qualified TEM sample, the following consecutive steps were conducted: (i) transferred the dendrites from the substrate (epoxy resin) to a conductive (and adhesive) carbon tape; (ii) found the dendrite on the carbon tape using scanning electron microscopy (ZEISS EVO MA 15 SEM) and then the dendrites were coated platinum to prevent them from collapsing; (iii) a very thin slice of platinum-coated dendrites were sectioned and further thinned using a site specific dual-beam focused ion beam (FIB) (FEI Helios Nanolab 600i) lift-out procedure [16]. In this work, a STEM lamella containing dendrites which were formed at 2.38 V vs. SCE was prepared. The bright-field TEM imaging was carried out by means of a JEOL 2200FS TEM operating at 200 kV accelerating voltage. Further STEM imaging and Energy Dispersive X-ray Spectroscopy (EDS) were conducted by a probe aberration-corrected TEM/STEM (FEI Titan Themis) with an acceleration voltage of 300 kV. For high angle annular dark-field (HAADF) imaging a probe semi-convergence angle of 17^{o} mrad and inner and outer semi-collection angles ranging from 73 to 200 mrad were selected.

3. Results and Discussion

3.1 Ions concentrations in the electrolyte

When a anodic polarization potential is applied on 96.5Sn-3Ag-0.5Cu alloy under a thin electrolyte layer containing 1 mM NaCl (Initial pH 6.7), it is expected that ions such as Sn^{2+}， Sn^{4+}, Cu^{2+}, Ag^{+} and OH^{-} may be generated. The cathodic reactions may include the reactions of O_2 reduction and H_2O reduction as following equations (1) and (2), respectively:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

The main anodic reactions are the dissolution of 96.5Sn-3Ag-0.5Cu alloy, possibly including the following reactions:

$$Sn \rightarrow Sn^{2+} + 2e^- \tag{3}$$

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^- \tag{4}$$

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{2+} + 2e^{-} \qquad (5)$$

$$\mathrm{Ag} \rightarrow \mathrm{Ag}^{+} + e^{-} \qquad (6)$$

Once these anodic reactions occur, metals ions will be produced and migrate in the electrolyte. Therefore, these ions in electrolyte could be detected using suitable instruments and methods if reactions (3)-(6) indeed occur during ECM process.

In this work, the ICP-MS was employed and the concentrations of tin ions (probably the mixture of Sn^{2+} and Sn^{4+}, Sn^{2+}/Sn^{4+}) [17], Cu^{2+} and Ag^{+} formed at different potentials are shown in Fig. 2. It can be seen that Sn^{2+}/Sn^{4+} can be detected at each selected potential and the concentration increases with the increasing potential (Fig. 2a). For example, the average concentration of Sn^{2+}/Sn^{4+} is about 1348.5 μg/L when -0.12 V vs. SCE was applied on the working electrode for 20 seconds. As the potential increases to 2.38 V vs. SCE, the average concentration of tin ions sharply increases to 46766.7 μg/L.

For comparison, the average concentration of Cu^{2+} at each potential was also detected, as shown in Fig. 2b. Like tin ions, the copper ions can be found at every potential and its average concentration increases from 51.2 μg/L to 1596.9 μg/L when the potential increases from -0.12 V vs. SCE to 2.38 V vs. SCE.

However, Ag^{+} concentration is zero at -0.12 V vs. SCE, as shown in Fig. 2c, indicating that intermetallic compound Ag_3Sn in 96.5Sn-3Ag-0.5Cu alloy did not dissolve into electrolyte at all. Even though the anodic polarization potential increases up to 0.38 V vs. SCE, the Ag^{+} could not still be detected. However, when the potential continued to increase to 2.38 V vs. SCE, Ag^{+} could be detected and its concentration is 3.9 μg/L. The presence of Ag^+ in the electrolyte means that Ag_3Sn could be dissolved at certain potential. These results undoubtedly indicate that Ag will at least participate the anodic dissolution process during the ECM of 96.5Sn-3Ag-0.5Cu alloy, but it is potential-dependent, i.e., the anodic polarization potential applied on 96.5Sn-3Ag-0.5Cu alloy should be high enough, otherwise, Ag_3Sn could not be dissolved and Ag will not participate the ECM process.

In addition, at each potential, it is obvious that the concentration of Sn^{2+}/Sn^{4+} is far higher than Cu^{2+} or Ag^+, demonstrating that Sn dominates the anodic dissolution process in ECM. This also suggests that Sn^{2+}/Sn^{4+} will play a significant role in the subsequent step of ECM of 96.5Sn-3Ag-0.5Cu alloy.

3.2 Composition of dendrites

The Ag^+ concentration detection demonstrates that Ag^+ can be found in electrolyte layer, although it is potential-dependent. According to definition of ECM, silver ions will migrate toward the cathode where they can be reduced to metallic dendrite and grows toward the anode. Therefore, it is necessary to examine the composition of dendrites for further clarifying Ag participating cathodic reduction process in ECM.

As mentioned above, the silver ions concentration is only 3.9 μg/L when 2.38 V vs. SCE was applied on the working electrode, however, the Sn^{2+}/Sn^{4+} concentration and Cu^{2+} concentration are as high as 46766.7 μg/L and 1596.9 μg/L, respectively. This means that the amount of Ag in dendrite will be very small even if the Ag^+ can be successfully deposited. Therefore, an accuracy detection technique is required. In this work, TEM was employed to analyze the composition of dendrites formed at 2.38 V vs. SCE since it shows the high accuracy in chemical distribution.

The results are shown in Figs. 3 and 4. For analyzing the composition distribution in more detail, one red region from Fig. 3c has been exemplarily cropped and magnified in Fig. 3d imaging by HAADF-STEM mode. STEM-EDS was performed and the results are displayed in Fig. 3e-h. It is confirmed that four principal elements, i.e., C, Sn, Cu and Ag, are distributed in the cross-section of dendrites. The presence of C could be attributed to the carbon conductive tape where the dendrites were stuck on. It is easily to understand the presence of Sn and Cu in dendrites since the Sn^{2+}/Sn^{4+} concentration and Cu^{2+} concentration in electrolyte layer are relative high, and most importantly, the potential on CE should be very negative because a very positive potential (2.38 V vs. SCE) was applied on WE. Simultaneously, the existences of Sn and Cu are also in good agreement with previous work [3-7]. Surprisingly, the Ag cannot only be detected, but also it co-exists with Sn and Cu at the corresponding areas, showing that the presence of Ag is not occasional, but it distributes widely. This results definitely demonstrate that Ag can participate the deposition process during the ECM under such a condition.

Fig. 4 shows a quantitative data of the three principle elements across the cross-section of dendrites marked by yellow arrows in Fig. 3d. The distribution of element along L1 and L2 also shows that Ag is present in the dendrite, but its amount is limited. It can easily understand that just small amount of Ag is seen since the average concentration of Ag^+ in electrolyte is just 3.9 μg/L which is far below the average ions concentration of Sn and Cu (Fig. 2). The TEM/STEM results undoubtedly prove that Ag can participate deposition process during the ECM of 96.5Sn-3Ag-0.5Cu alloy.

3.3 Migration process of Ag on the ECM of 96.5Sn-3Ag-0.5Cu alloy

The migration of Ag in 96.5Sn-3Ag-0.5Cu alloy is different from pure Ag which is considered as one of the most susceptible metals to ECM [18]. The results of ICP-MS demonstrate that the presence of Ag^+ depends upon the anodic polarization potential during the ECM of 96.5Sn-3Ag-0.5Cu alloy (Fig. 2). Once the potential is high enough to make the Ag in Ag_3Sn dissolved, the silver ions can be detected in electrolyte and the Ag element can also be found in dendrites (Figs. 3 and 4).

As soon as the Ag dissolves from Ag_3Sn, the Ag^+ ions will be formed as described by reaction (6). At the same time, the OH^- will be produced at cathode because of the O_2 reduction and H_2O reduction, as expressed in reactions (1) and (2). Then, the Ag^+ will migrate toward that cathode and OH^- will migrate toward anode. Once both types of ions meet together, Ag^+ then combine with OH^- to form AgOH which is not stable and decomposes to Ag_2O and H_2O according to the follow equilibrium [19]:

$$2Ag^+ + 2OH^- \leftrightarrow 2AgOH \leftrightarrow Ag_2O + H_2O \tag{7}$$

The colloid precipitate of Ag_2O can easily be reduced to metal Ag at cathode. At the same time, the Ag^+ can also migrate toward the cathode where electrochemical deposition occurs:

$$Ag^+ + e^- \rightarrow Ag \tag{8}$$

Consequently, the Ag can be found in the dendrites during the ECM of 96.5Sn-3Ag-0.5Cu alloy.

4. Conclusions

Ag participating the ECM of 96.5Sn-3Ag-0.5Cu alloy was clarified in this work. The presence or absence of Ag^+ in the electrolyte layer during ECM strongly depends upon the anodic polarization potential. E.g., Ag^+ could not be detected at the -0.12 V vs. SCE and 0.38 V vs. SCE, but it can be found at 2.38 V vs. SCE. Moreover, Ag could also be found in dendrites formed at 2.38 V vs. SCE. The distribution of Ag in dendrite is not occasional, but widely co-existed with Sn and Cu. Therefore, it is confirmed that Ag can participate the ECM of 96.5Sn-3Ag-0.5Cu alloy, but it is potential-dependent.

Acknowledgements

This work supported by National Science Foundation of China [grant number 51601159], Application and Fundamental Research of Sichuan Province [grant number 2017JY0171], and Scientific and Technological Innovation Team for the Safety of Petroleum Tubular Goods in Southwest Petroleum University [grant number

2018CXTD01]. Bálint Medgyes would like to thank the support for the National Research, Development and Innovation Office – NKFIH [grant number PD 120898].

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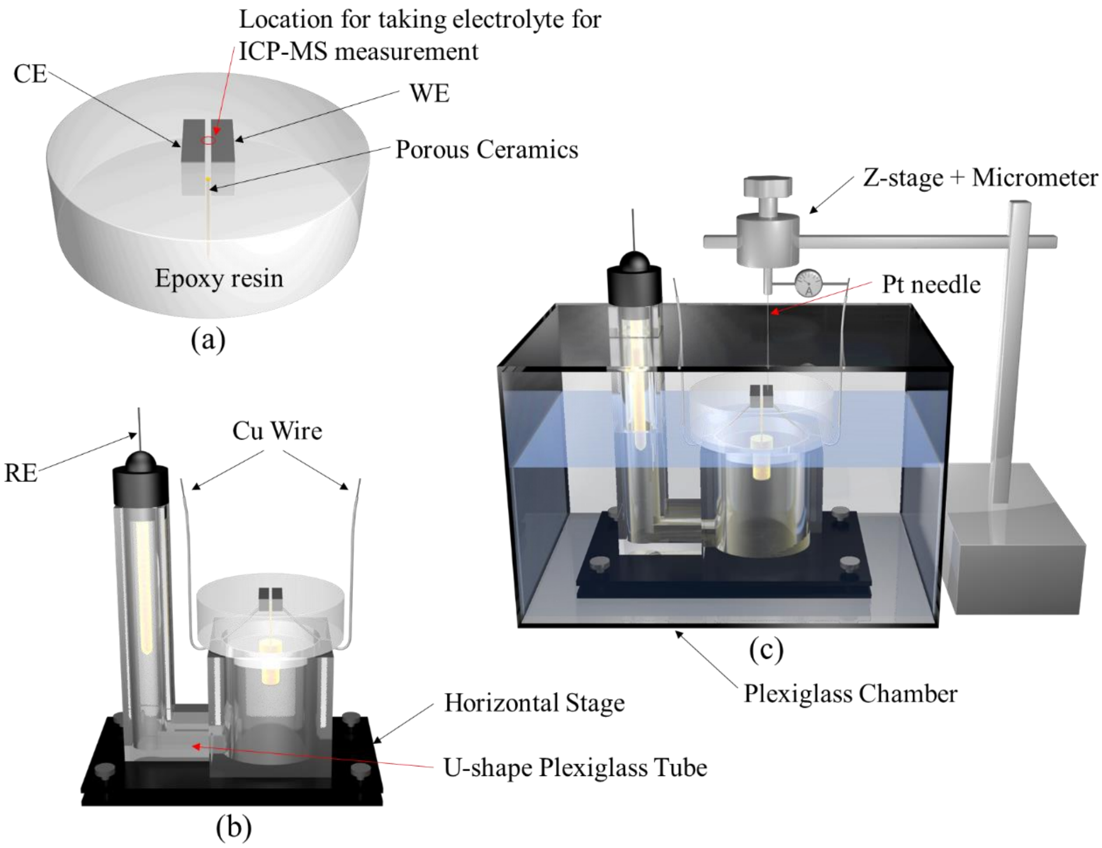

Fig. 1. Schematic diagrams: (a) electrodes embedded in epoxy resin, (b) electrodes connected with U-shape plexiglass tube on the horizontal stage and (c) the whole setup for electrochemical migration test.

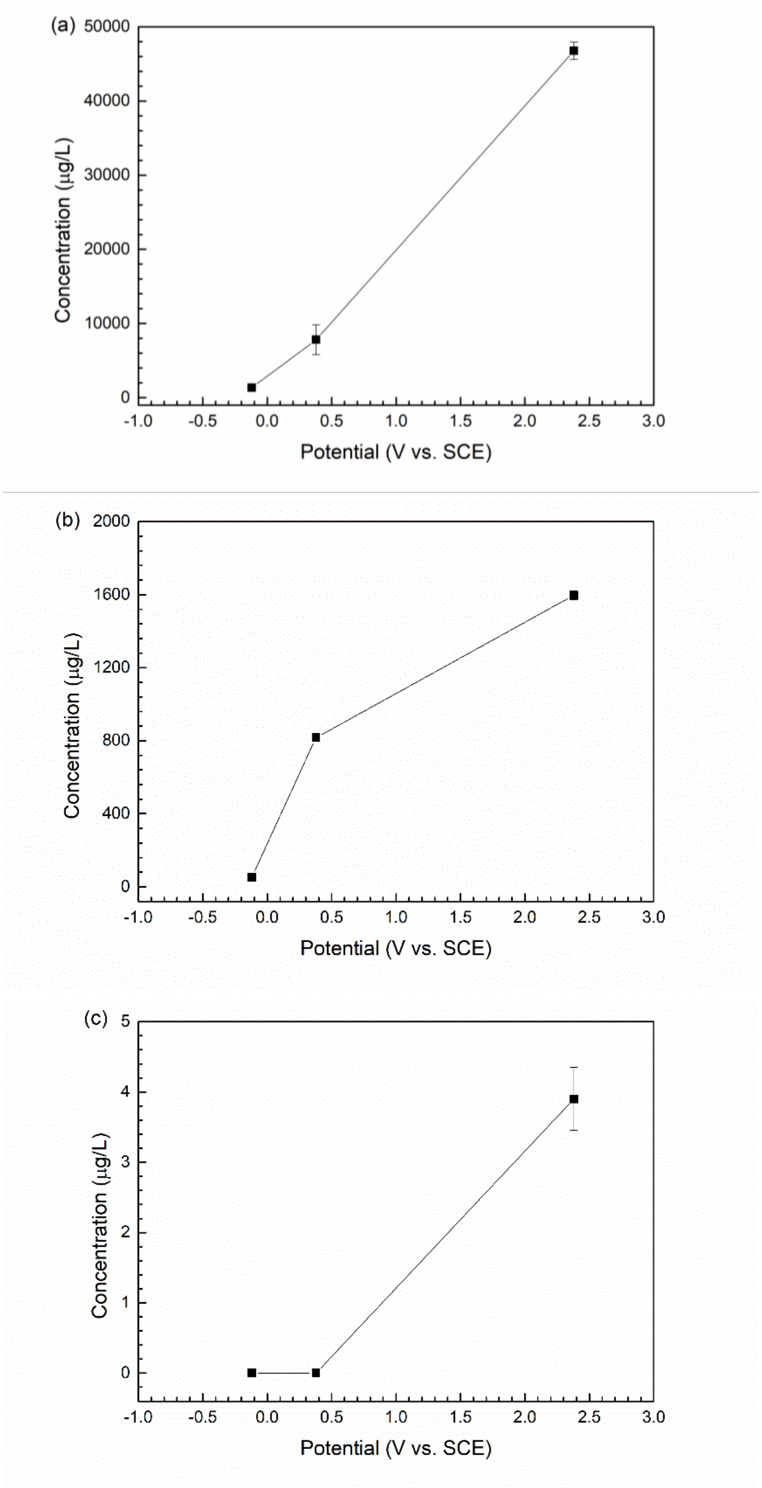

Fig. 2. The concentration of ions in the electrolyte layer after 20 seconds of ECM test of 96.5Sn-3Ag-0.5Cu alloy under different potential with respect to SCE: (a) Sn^{2+}/Sn^{4+}, (b) Cu^{2+} and (c) Ag^{+}. The error bars indicate standard deviation.

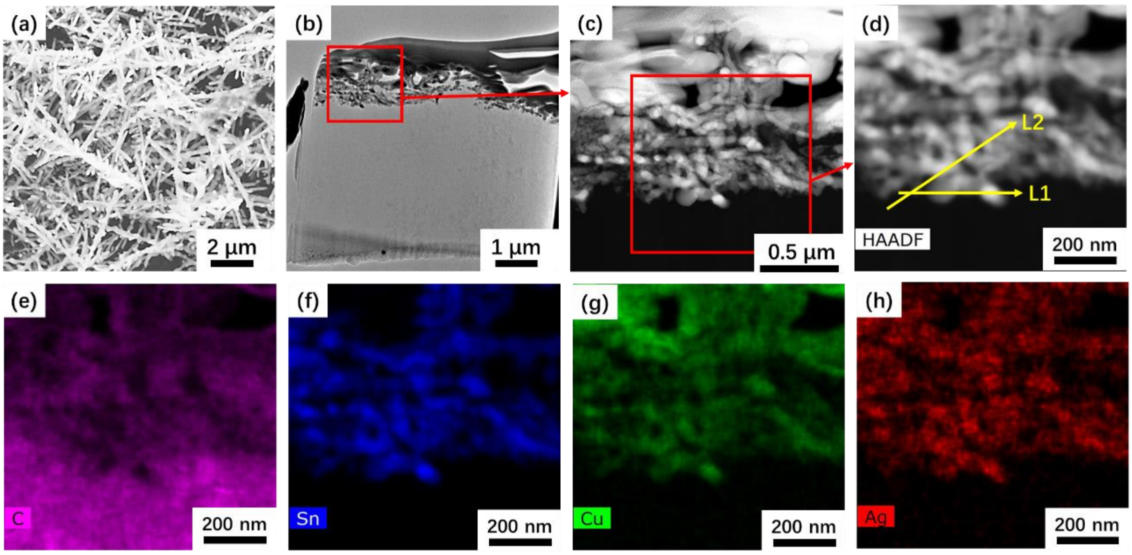

Fig. 3. SEM/TEM/STEM analysis of dendrites formed in the ECM of 96.5Sn-3Ag-0.5Cu alloy under 2.38 V vs. SCE, (a) SEM image of dendrites surface, (b) low magnification SEM, (c) bright field TEM, (d) high resolution HAADF-STEM, (e-h) STEM-EDS maps with the identical sample region in (d) showing the distributions of the four principle elements, i.e., C, Sn, Cu and Ag.

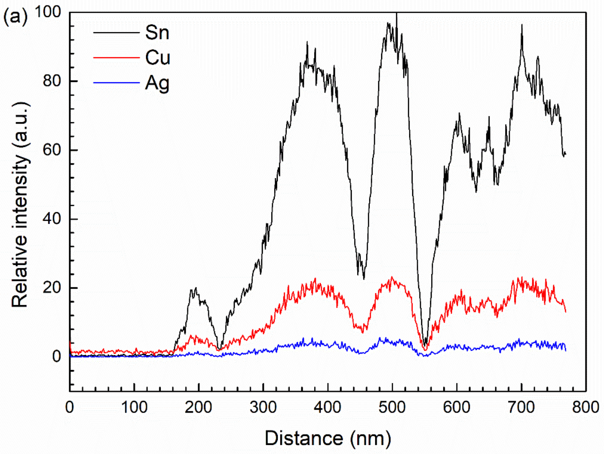

Fig. 4. TEM/EDS line scan conducted along the arrow marked in Fig. 3d, (a) L1 in Fig. 3d and (b) L2 in Fig. 3d. The dendrites formed in the ECM of 96.5Sn-3Ag-0.5Cu alloy under 2.38 V vs. SCE.