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Composition and structure of Al-Sn alloys formed by constant potential electrolysis in an $AlCl_3$-NaCl-KCl-$SnCl_2$ molten salt

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Abstract

To form Al-Sn alloys for bearing materials, molten salt electrolysis was performed in an $AlCl_3$-NaCl-KCl molten salt containing $SnCl_2$ at 423 K. The voltammogram showed that the cathodic reduction of the Sn ions started at a potential of 0.5 V vs. Al/Al(III) in the molten salt showing that deposition of pure Sn was possible at 0.5 V. Co-deposition of Al and Sn occurred at potentials more negative than 0.1 V. The co-deposit was composed a solid solution of Al and Sn. The ratio of the Sn in the electrodeposits decreased with the potential from 100 at% at 0.2 V to 19 at% at -0.3 V. In the structural observations, electrodeposits with an alternate stacked structure of Al and Sn is obtained at -0.075V.

Keywords: molten salt, Al-Sn alloy, electrodeposition, bearing materials

1. Introduction

Al-Sn alloys are simple eutectic binary alloy systems with solid solutions of a wide range of compositions[1] and are well known as lubricating compounds, with the Al-Sn used as a surface coating for sliding bearings.[2] The alloys also excel in high temperature stability. The surface finishing of the bearings is provided by dip coating or sputtering in industrial applications. Anil et al. and Perrone et al. have reported the formation of Al-Sn alloys by spray deposition and pulse laser ablation techniques.[3,4] A drawback of present production processes is the need for expensive apparatus.

We have proposed a resistive coating of Al alloy layers produced by electroplating on the substrate from molten salts.[5-7] To prepare a uniform and thin coating on the substrate with low production costs, electrolysis was applied in a low-temperature molten salt for the formation of the coating. There have been a number of papers on the formation of alloy electrodeposits of Al-Cr, Al-Ni, Al-Mn, and Al-Ti from low-temperature molten salts[8-13]; however, no papers of electrodeposition of Al-Sn alloys have been located. In the study here, the electrodeposition of Al-Sn alloys from $AlCl_3$-NaCl-KCl molten salt containing $SnCl_2$ at 423 K is reported. The relation between the alloy composition and electrolysis potential is examined, and the relationship between the structure of the electrodeposits and alloy composition are discussed.

2. Experimental

Tin chloride ($SnCl_2$, Wako pure chemical, 99.99% pure) was used as received. A mixture of 61 mol% aluminum chloride (Furuka, 99.8% pure), 26 mol% sodium chloride (Wako pure chemical, 99.9% pure), and 13 mol% potassium chloride (Wako

pure chemical, 99.9% pure) were melted at 423 K and pure aluminum was immersed in the melt for longer than 4 days. The electrochemical cell was a Pyrex glass cylinder covered with a wire heater. A glassy carbon (GC, Tokai carbon, GC-20) plate with a surface area of 3 cm^2 and a pure tin plate (Niraco, 99.9% pure, 12 cm^2) were used as the working electrode and counter electrode, respectively. Pure aluminum wire (Niraco, 99.99% pure) placed in a small Pyrex glass tube filled with the $AlCl_3$- NaCl- KCl melt was used as the reference electrode. To maintain electrical contact between the electrolyte melt and the reference electrode, a ceramic fiber was inserted through a hole at the bottom of the tube. The $SnCl_2$, at a concentration of 0.05 $moldm^{-3}$ (M) was added to the $AlCl_3$- NaCl- KCl melt, and the potential during the electrolysis was controlled by a Hokuto-Denko HZ-5000 potentiostat.

Voltammograms were measured at a potential range from 0.8 to –0.2 V vs. Al/Al(III) with a scan rate of 5.0 x 10^{-3} V s^{-1} in the molten salt containing $SnCl_2$. Electrodeposited films of Al-Sn alloys were formed on the GC electrode at constant potentials in the range from 0.4 to -0.3 V in the molten salt with a charge density of 40 Ccm^{-2}. The formed electrodeposits were analyzed by electron probe micro analysis and observed by scanning electron microscopy (EPMA, JEOL JXA-8900M), X-ray diffraction (XRD, JEOL JDX-3500, Cu-Kα radiation), and fluorescence X-ray spectroscopy (JEOL JSX-3220Z, Rh target).

3. Results and Discussion

3.1 Voltammogram measurements

A voltammogram of the molten salt is shown in Fig. 1, here the potential is scanned from 0.8 V to –0.2 V at a sweep rate of 5 x 10^{-3} V s^{-1} on the glassy carbon electrode in the $AlCl_3$-NaCl-KCl melt with or without $SnCl_2$. In the melt without $SnCl_2$ the

voltammogram indicates a steep increase of current at potentials lower than 0.0 V (solid line in the figure). In the reverse scan, an anodic current was observed from 0.0 V. The cathodic and anodic currents correspond to Al deposition and dissolution reactions.

The voltammogram of the melt containing $SnCl_2$ shows a small cathodic current at potentials from 0.5 V to 0.0 V (dotted line in the figure). Since there is no cathodic current in this region of the voltammogram in the $AlCl_3$-NaCl-KCl melt without $SnCl_2$, the current around 0.5 V may be attributed to electrodeposition of Sn from Sn^{2+}. The cathodic current increases sharply at potentials below 0.0 V. The main contributor to the current in this region may be due to the electrodeposition of Al.

When the potential is reversed at -0.2 V, a large anodic current appears from 0.0 V to 0.2 V and a small anodic current flows again from 0.4 to 0.6 V. The anodic current at around 0.1 V and 0.5 V corresponds to anodic dissolution of the electrodeposits formed by the previous cathodic scan. The anodic reaction at around 0.1 V in the molten salt including $SnCl_2$ arises from a dissolution of the Al-Sn alloy deposit. The anodic reaction at around 0.5 V may result from a dissolution of the Sn in the deposit.

3.2 Relation between potential and composition in constant potential electrolysis

Electrodeposition of Al-Sn alloy was carried out on copper substrate at different potentials from -0.3 to 0.3 V at 40 Ccm^{-2} in a melt containing $SnCl_2$, to examine the influence of the potential on the composition of the deposited compounds.

The colors of the electrodeposit were bright grey from -0.3 to -0.1 and dark grey at potentials above 0.0 V. The composition of the electrodeposits formed under the constant potential control was analyzed by fluorescence X-ray spectroscopy, and the Sn concentrations in the deposits are shown in Fig. 2 as a function of the potential. The

concentration of Sn increases steeply from -0.2 to 0.1 V, and the electrodeposit formed at 0.3 V was composed of only Sn. In the voltammogram of Fig. 1, it was expected that Al electrodeposition mainly occurs at potentials below 0.0 V, however the Sn concentration in the electrodeposit was about 19 at% at a potential of -0.3 V. We have observed that when pure Al plate is immersed for a few seconds into the molten salt used here, Sn formed on the Al plate by an exchange reaction between the Al and Sn ions in the electrolyte (data not shown). Therefore, an exchange reaction must be considered to occur during the electrolysis and after the electrolysis in this experiment and the Sn deposit resulting from this exchange reaction may be included in the 19 at% Sn recorded at -0.3 V.

Figure 3 (a)-(c) shows surface and cross sectional SEM images of electrodeposits formed at -0.15, -0.075, and 0.2 V, respectively. In the SEM images, bright and dark colors show Sn and Al, the composition of the electrodeposits at (a), (b), and (c) are 21, 32 at% Sn-Al, and 100 at% Sn, respectively. The surface image of Fig. 3(a), shows linearly arranged Al electrodeposits of about 5 μm width, with a net-like white pattern of Sn on the linear Al deposits. In the cross sectional image of Fig. 3(a), extended longitudinal white Sn deposit extend from the substrate to the surface of the deposit. In the surface image in the top panel of Fig. 3(b), it is seen that white Sn deposits cover much of the Al deposit. In the cross sectional image of Fig. 3(b), the Al and Sn deposits are stacked in an alternating layer-like structure. In the surface image of Fig. 3(c), there are granular Sn deposits, and spherical Sn deposits are observed in the cross sectional image.

Figure 4 shows the XRD pattern of the electrodeposit formed at potentials at 0.075 V, showing diffraction patterns of metallic Al, β-Sn, and the Cu of the substrate. The

diffraction patterns of the electrodeposit formed at other potentials were very similar to those in Fig. 4. The XRD results indicate that the electrodeposits of the Al-Sn alloys consist of crystalline Al and β-Sn.

3.3 Mechanism of structure formation in Al-Sn electrodeposits

A net-like white pattern of Sn is formed on the Al deposit as shown in the top panels of Fig. 3 (a) and (b). Formation of this pattern can be related to the deposition mechanism of the Al and Sn. An illustration of the formation mechanism suggested by the observations is shown in Fig. 5(a) and (b), for the deposits at -0.15 and -0.075V, respectively. In Fig. 5(a), a small number of Sn and large number of Al nuclei are initially deposited on the substrate as Al electrodeposition occurs more easily in this potential (-0.15V). Then, Al and Sn atoms deposit on these nuclei and there is surface diffusion of the atoms. Since atoms move to stable sites on the surface, the Al and Sn atoms would remain on the sites with already deposited Al and the Sn, respectively. This could be the reason for the striped structure like in Fig. 3 (a) forming on the substrate.

In Fig. 5(b) at -0.075 V, there is more electrodeposition of Sn than at -0.15V in Fig. 5 (a), and the following will discuss the mechanisms of two types electrodeposition.

(1) Co-deposition of the Al atoms and Sn atoms occurs on the surface, as well as there is surface diffusion of the atoms that are deposited. However since the atoms are in an immiscible binary alloy system, the atoms become separated into Al and Sn phases in the surface diffusion. The result may develop into the alternating stacked structure of Al and Sn suggested in Fig. 5(b), and observed in Fig. 3(b).

(2) During the electrodeposition of Al and Sn, there is an exchange reaction between the surface of the electrodeposited Al and Sn ions in the molten salt and a Sn layer is

formed on the electrodeposited Al. A repeated electrodeposition and exchange reaction may then result in the alternating stacked structure of Al and Sn. However, there is no conclusive evidence for these two mechanisms and we are currently studying this matter future.

At 0.2 V, the deposit is composed of pure Sn, and as the melting point of Sn at 505 K is close to the temperature of the molten salt at 423 K, the shape of the electrodeposit becomes spherical.

In the use the Al-Sn alloy as a bearing material, a striped (alternating) structure of soft Sn metal and harder Al is desirable and, therefore, electrodeposits like those in Fig. 3(b) would be a candidate for compounds.

4. Conclusions

To form Al-Sn alloys intended as compounds for bearing, pure Sn and Al-Sn alloys with a variety of compositions were electrodeposited by constant potential electrolysis in 61 mol% $AlCl_3$- 26 mol% NaCl- 13 mol% KCl containing $SnCl_2$ at 423 K.

The results may be summarized as follows:

(1) Cathodic reduction of Sn ions starts at potentials of 0.5 V vs. Al/Al(III) and alloys of Al-Sn are deposited at potentials lower than 0.2 V in the molten salt.

(2) The Sn concentration of the electrodeposit increases from 19 at% at -0.3V to 100 at% at 0.2 V when the deposition was performed under constant potential control.

(3) The compositions of the Al-Sn electrodeposits were crystalline Al and β-Sn as shown by XRD analysis.

(4) An electrodeposit with an alternating stacked structure of Al and Sn is obtained at -0.075V. This may be due to a combination of electrodeposition of Al, Sn, and

an exchange reaction between Al electrodeposits and Sn ions in the electrolyte.

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Figure and captions

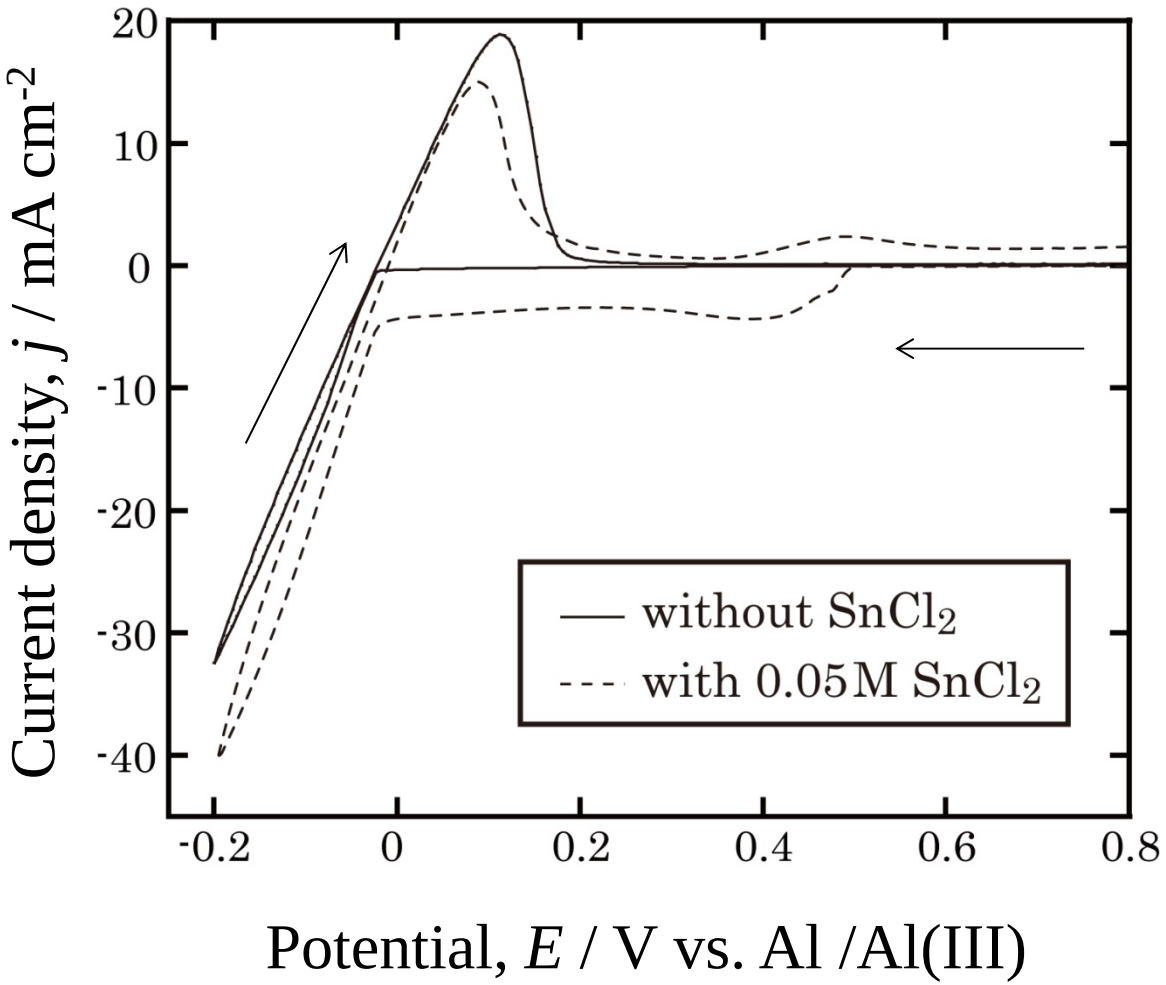
Fig. 1 Voltammogram of the GC electrode in the $AlCl_3$-NaCl-KCl molten salt containing $SnCl_2$.

Fig. 2 Concentration of Sn in the electrodeposit as a function of the potential of the electrolysis.

Fig. 3 SEM images of surface and cross sections of electrodeposits formed at: (a) -0.15 V, (b) -0.075V, and (c) 0.2 V.

Fig. 4 XRD patterns of electrodeposits formed at a potential of -0.075 V.

Fig. 5 Schematic illustration of the structure of the formed electrodeposits. Electrolysis potential, (a) -0.15 and (b)-0.075V.



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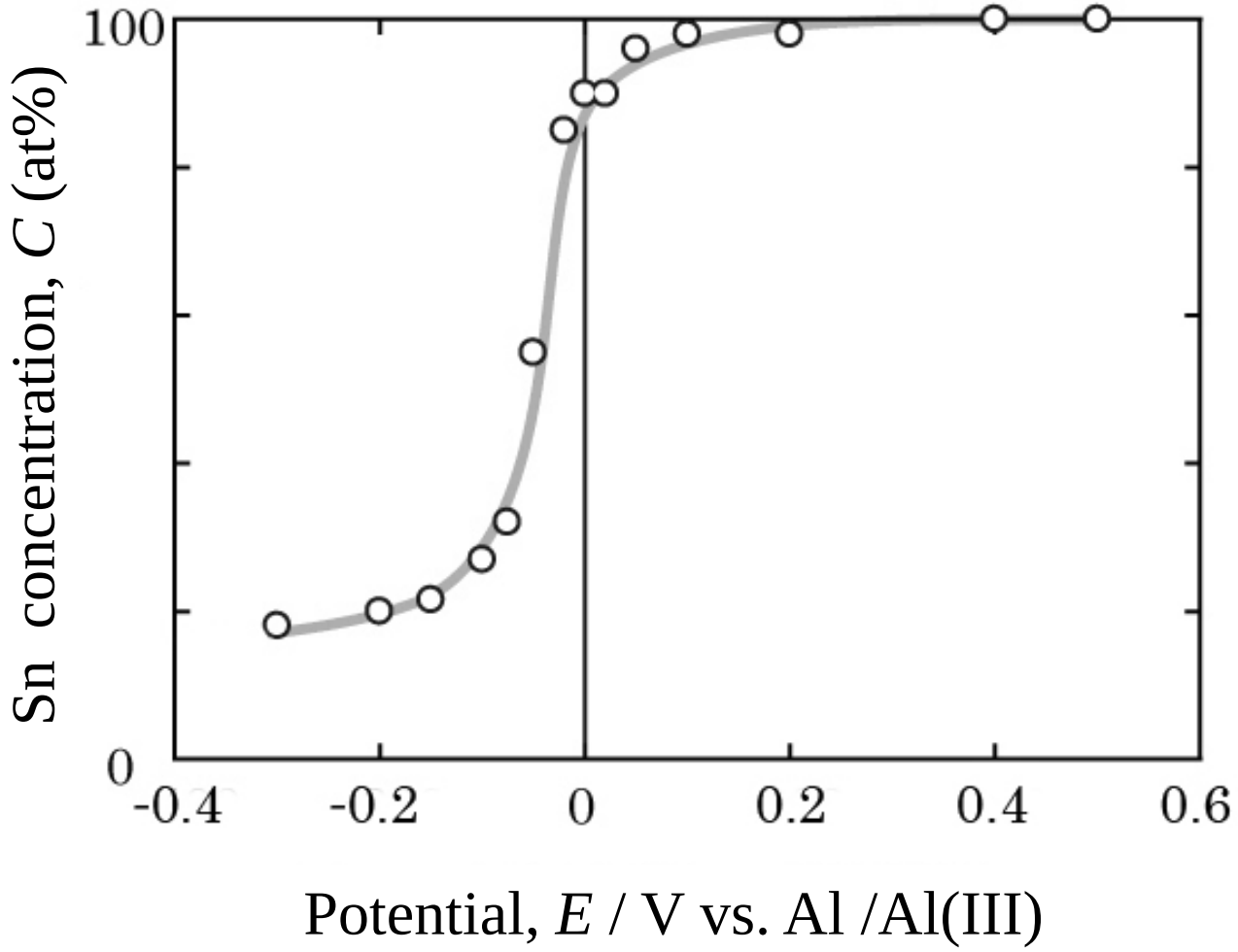

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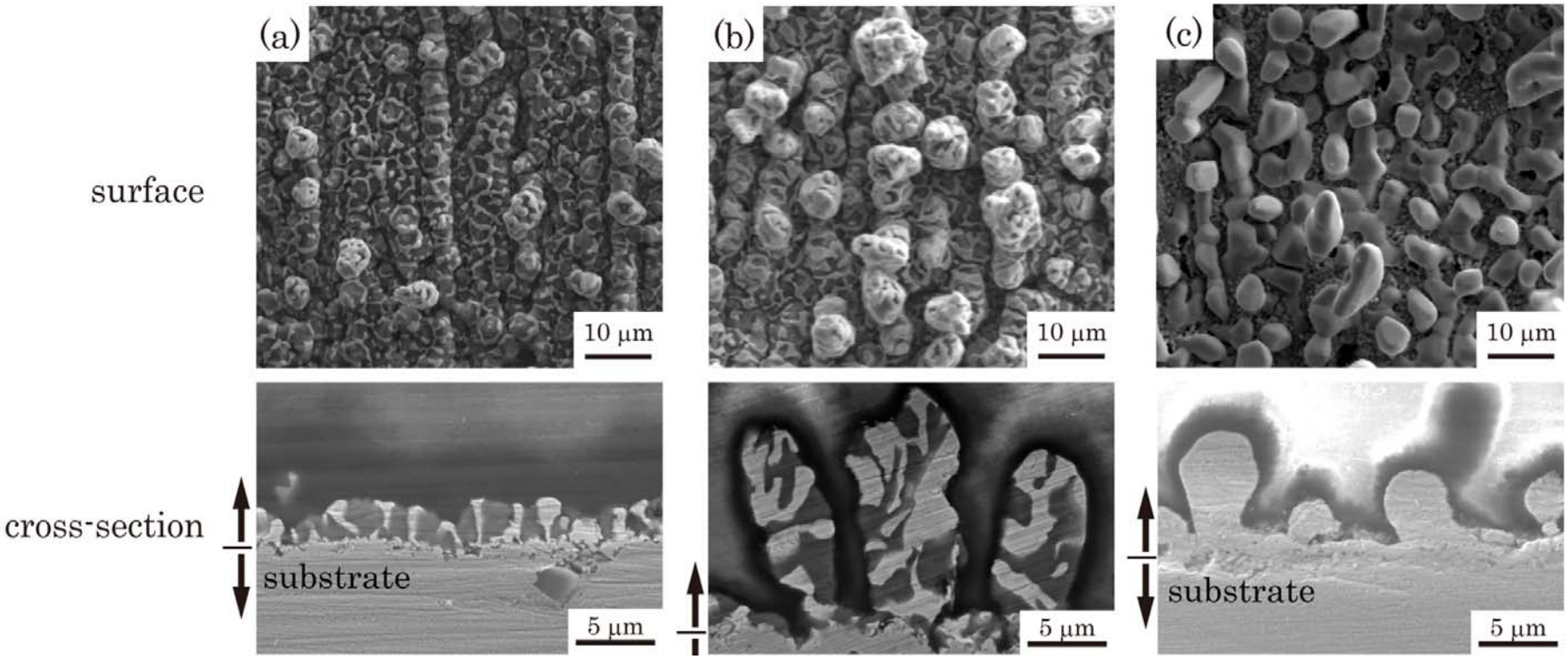

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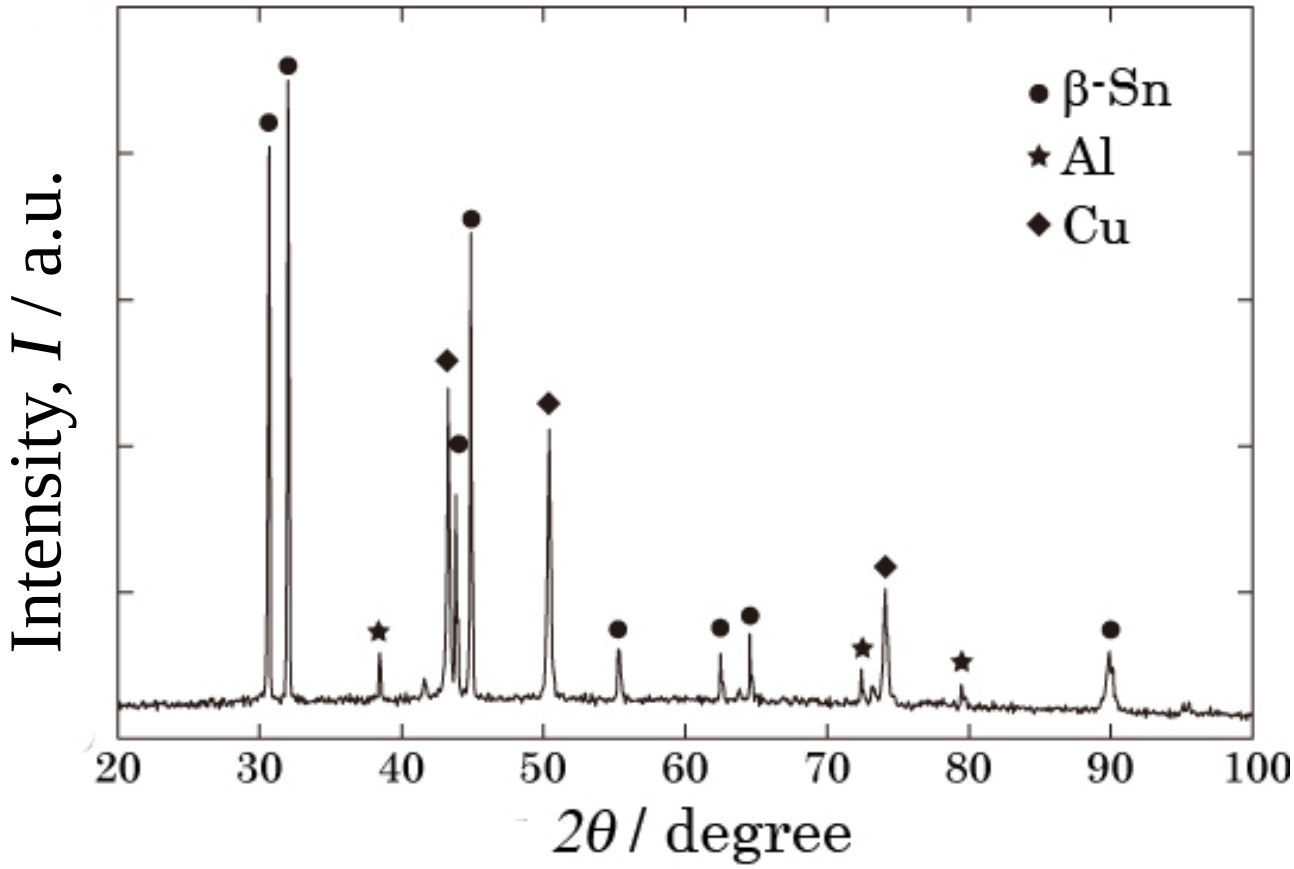

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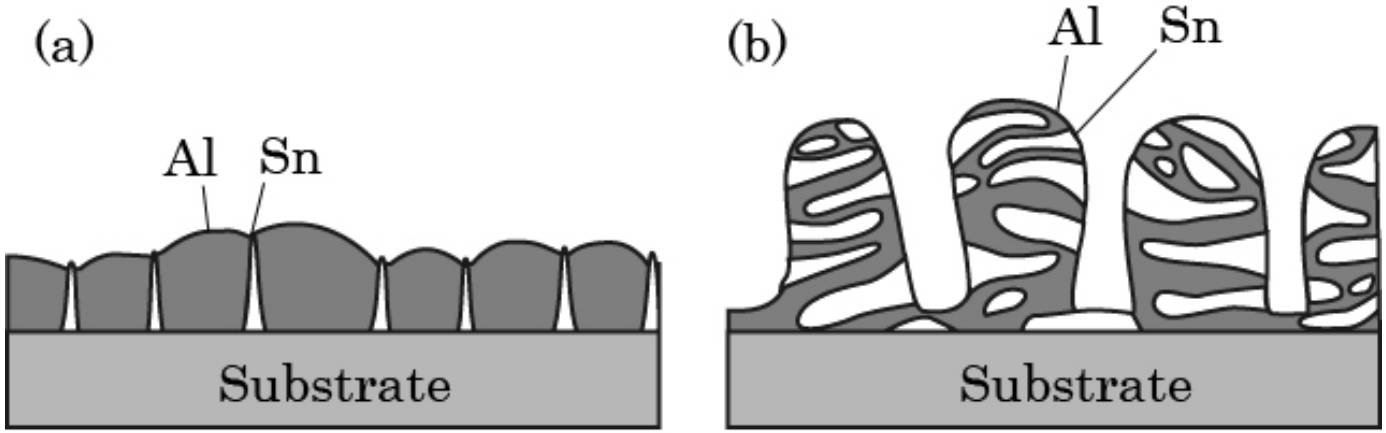

Fig. 5 Schematic illustration of the structure of the formed electrodeposits. Electrolysis potential, (a) -0.15 and (b)-0.075V.