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Electrodeposition of Sb-Te Alloy in $AlCl_3$-NaCl-KCl Molten Salt

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The Electrodeposition of Sb-Te alloy was carried out in $AlCl_3$-NaCl-KCl molten salt containing $SbCl_3$ and $TeCl_4$ at 423 K by constant potential electrolysis. The voltammogram on a glassy carbon (GC) electrode in a melt containing 1.0×10^{-2} kmol m^{-3} $SbCl_3$ and 1.0×10^{-2} kmol/m^3 $TeCl_4$ revealed the cathodic current waves at 1.5, 1.1, and 0.9 V vs. Al/Al(III). A stable Sb-Te alloy deposit was obtained at 0.85 V in the melt containing $SbCl_3$ and $TeCl_4$. At the higher concentration ratio of the Sb(III) to (Sb(III) + Te(IV)), a good linear relation was found between the atomic ratio of Sb in the deposit and the concentration ratio of Sb (III) in the melt. The Sb-Te alloy deposit of atomic ratio of 38 : 62% which was assume to be suitable for a thermoelectric device was obtained with the molten salt containing 7.0×10^{-3} kmol/m^3 $SbCl_3$ and 1.0×10^{-2} kmol/m^3 $TeCl_4$. The XRD pattern of the deposit corresponds to that of Sb_2Te_3 intermetallic compound. The deposit had homogeneous disk-like granule with the disk size of about 10 µm. [doi:10.2320/matertrans.E-MRA2008811]

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1. Introduction

Compound semiconductors such as antimony telluride (Sb_2Te_3), bismuth telluride (Bi_2Te_3) and silicon germanium (SiGe) have the properties of thermoelectric cooling (Peltier effect) and thermoelectric generation (Seebeck effect). At the present Bi_2Te_3 has been widely employed in the thermoelectric devices operated at room temperature as the cooling systems of refrigerator, Freon-free air conditioners, and wine cellars.

The Sb_2Te_3 intermetallic compound behaves as a memory medium and thermoelectric device.[1)] Several methods for preparation of Sb_2Te_3 such as melting method,[2)] MOCVD,[3)] and Co-evaporation method[4)] have been reported. Electrodeposition has been also reported for the preparation of Sb_2Te_3.[5)] The electrochemical method has a number of advantages over the other methods: (1) easy control of the composition by the potential applied, (2) easy control of film thickness by the electric charge applied, (3) low cost, and (4) simple manufacturing process. We further suppose that the crystallinity of deposits is more enhanced by the electrolysis in $AlCl_3$-NaCl-KCl molten salt which is operated at temperature of 423 K than by the electrolysis in aqueous solutions at room temperature. In the present paper, we examine the electrodeposition of Sb-Te alloys in $AlCl_3$-NaCl-KCl molten salt containing $TeCl_4$ at a concentration of 1.0×10^{-2} kmol/m^3 and at various $SbCl_3$ concentrations. It will be reported that the composition of the deposit is successfully controlled by the change of Sb(III) concentration in the melt.

2. Experimental

Sodium chloride (NaCl, Wako pure chemical industries, 99.5% pure), potassium chloride (KCl, Wako pure chemical industries, 99.5% pure), anhydrous antimony chloride ($SbCl_3$, Aldrich, 99.999% pure), and anhydrous tellurium chloride ($TeCl_4$, Aldrich, 99.999% pure) were used as received. Aluminum chloride ($AlCl_3$, Fluka, 99.0% pure) was purified by the pre-electrolysis process to remove the impurities. A Pyrex glass cell was used for the electrodeposition. Schematic illustration of the cell is shown in Fig. 1, in which $AlCl_3$, NaCl, and KCl in a molar ratio of 61 : 26 : 13 with 50 ml volume were mixed and melted at 423 K. $SbCl_3$ and $TeCl_4$ were added to the melt at given concentrations. A glassy carbon plate (GC, Tokai carbon, GC-20SS) was used as the working electrode and as the counter electrode. A pure aluminum wire (Niraco, 99.98%, $\phi = 0.5$ mm) placed in small Pyrex glass tube was immersed in $AlCl_3$-NaCl-KCl molten salt and used as the reference electrode. To maintain electric contact between the electrolyte melt and the reference electrode, a small hole was made by insertion of asbestos fibers at the bottom of the tube. Electrochemical measurements were performed with a Hokuto-Denko HAG-5010 potentiostat in Ar gas atmosphere at 423 K.

Voltammogram was measured at potential from 1.8 to 0.2 V vs. Al/Al(III) with scan rate of 0.01 V s^{-1} in the molten salt containing $SbCl_3$ and $TeCl_4$. Electrodeposition films of

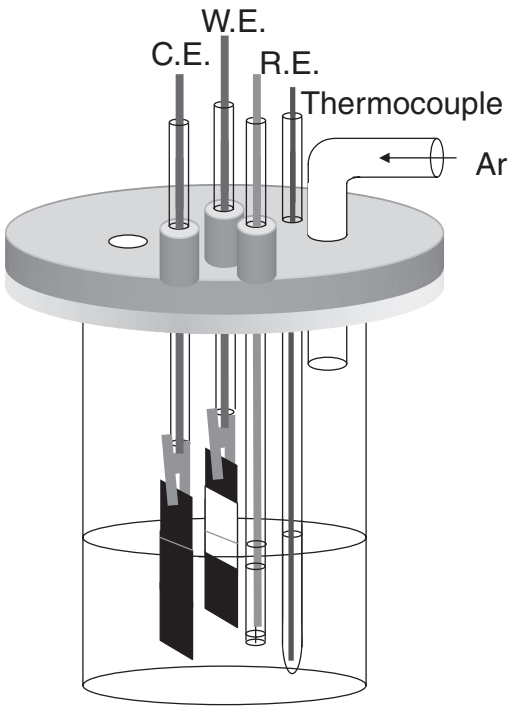


Fig. 1 Schematic illustration of electrochemical cell.

Sb-Te alloys were prepared at a constant electric charge of $4 \times 10^5\,C\,m^{-2}$ on the GC electrode.

The composition, the crystal structure, and the morphology of the deposits were analyzed by wavelength dispersive X-ray spectroscopy (WDX) (JEOL JXA-8900M, acceleration voltage:15 kV), X-ray diffraction (XRD, JEOL JDX-3500, Cu-Kα radiation), and scanning electron microscopy (SEM, JEOL JXA-8900M), respectively.

3. Results

The redox behaviors of Sb/Sb ions and Te/Te ions were reported by our previous paper.[6] In the paper, the reduction currents of Sb ions and Te ions were detected in the potential region between 0.2–1.5 V where these metals were deposited without any deposition of Al. The voltammogram and electrodeposition were therefore, carried out in this potential region.

The voltammogram of Sb(III) ion at $1.0 \times 10^{-2}\,kmol/m^3$ and Te(IV) ions at $1.0 \times 10^{-2}\,kmol/m^3$ in the melt on the GC electrode is shown in Fig. 2 in which the potential sweep was done a rate of $0.01\,V\,s^{-1}$ from 1.8 V to 0.2 V in the cathodic direction and the reverse from 0.2 V to 1.8 V in the anodic direction. The voltammogram shows cathodic waves at 1.5, 1.1, and 0.9 V vs. Al/Al(III) and anodic waves at 1.0, 1.2, and 1.3 V. During the cathodic sweep, purple fog was generated on the GC electrode at 1.5 V, and grey electrodeposit with the purple fog was observed on the electrode at about 1.1 V, however, the purple fog disappeared at about 0.9 V. During the anodic sweep, the purple fog was also seen in the potentials from 1.0–1.8 V, electrodeposit had formed on the electrode during the cathodic scan completely dissolved at 1.8 V.

Cathodic voltammograms in the melt containing of Sb (III) at concentration of 2.5×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, and $2.0 \times 10^{-2}\,kmol/m^3$ and Te (IV) at $1.0 \times 10^{-2}\,kmol/m^3$ in the melt are shown in Fig. 3. In Fig. 3, three reduction waves are observed at the potentials at about 1.5, 1.1, and 0.8–0.9 V, respectively. The cathodic currents of the waves at 1.1 and 1.5 V don't change with the concentration of Sb(III); however, the current at 0.8–0.9 V wave linearly increases with increase of the Sb (III) concentration.

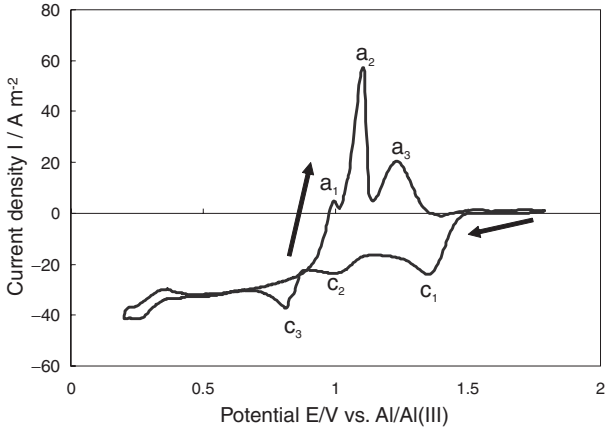


Fig. 2 Voltammogram on the GC electrode in $AlCl_3$-NaCl-KCl molten salt containing $1.0 \times 10^{-2}\,kmol/m^3$ $SbCl_3$ and $1.0 \times 10^{-2}\,kmol/m^3$ $TeCl_4$.

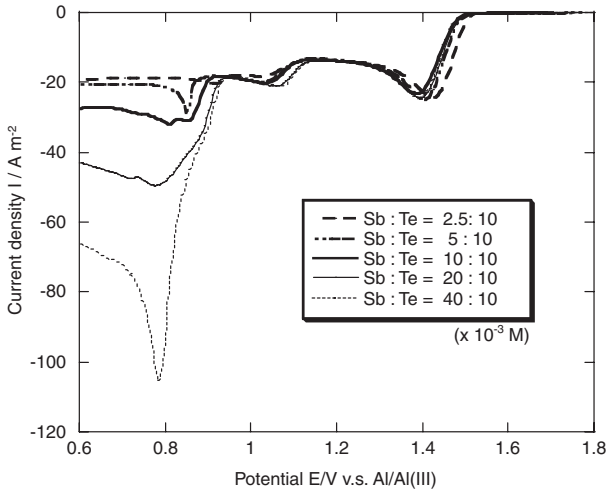


Fig. 3 Cathodic voltammograms in $AlCl_3$-NaCl-KCl molten salt containing various concentrations of Sb (III) and Te (IV) in the melt.

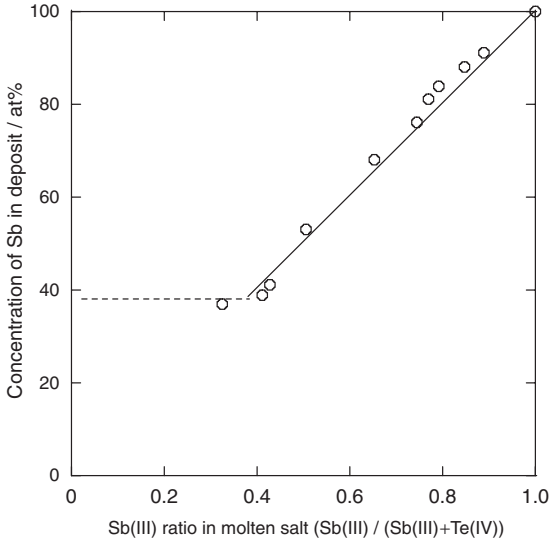


Fig. 4 Relationship between the concentration of Sb in the deposit and the concentration ratio of Sb (III) in molten salt.

When the electrodeposition was done at various potentials in the melt at a fixed concentration ratio of Sb(III) to (Sb (III) + Te (IV)), the concentration ratio of the deposit was almost constant, independent of the potentials. The atomic ratio was, however, changed with the concentration ratio of Sb (III) and Te (IV) in the melt.

Figure 4 shows a relationship between the concentration ratio of Sb(III) to (Sb (III) + Te (IV)) in the melt and the concentration ratio of Sb to (Sb + Te) in the deposit formed at 0.85 V. In the Fig. 4, the concentration of Te(IV) was constant at $1.0 \times 10^{-2}\,kmol/m^3$ and that of Sb(III) was charged from $4 \times 10^{-3}\,kmol/m^3$ to $9.0 \times 10^{-2}\,kmol/m^3$. It is seen that there is a linear relation between the Sb concentration in the deposit and the concentration ratio in the melt at the range of the concentration ratio more than 0.4. In the ratio of less than 0.4, the Sb concentration in the electrodeposits became constant at about 40 at%. On the electrodeposition in the melt at the ratio less than 0.4, the purple fog evolved from the GC electrode.

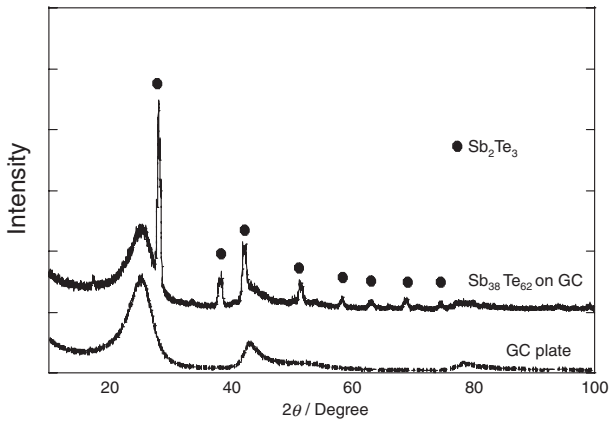


Fig. 5 XRD of the deposit formed in $AlCl_3$-NaCl-KCl molten salt containing 7.0×10^{-3} kmol/m^3 $SbCl_3$ and 1.0×10^{-2} kmol/m^3 $TeCl_4$ at 0.85 V. The XRD of the GC electrode is shown in the lower part for the comparison.

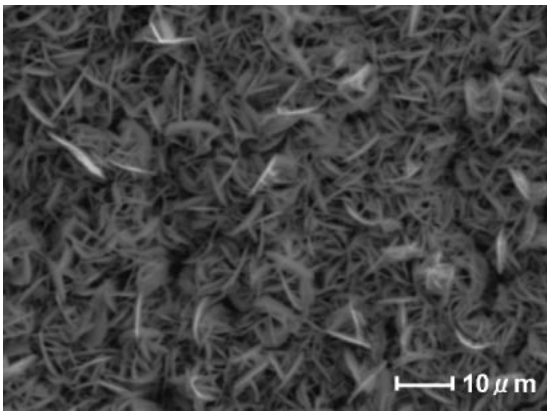


Fig. 6 SEM photograph of the deposit formed in $AlCl_3$-NaCl-KCl molten salt containing 7.0×10^{-3} kmol/m^3 $SbCl_3$ and 1.0×10^{-2} kmol/m^3 $TeCl_4$ at 0.85 V.

The XRD pattern of the 38 at%Sb-62%Te formed at 0.85 V in the molten salt containing 7.0×10^{-3} kmol/m^3 $SbCl_3$ and 1.0×10^{-2} kmol/m^3 $TeCl_4$. is shown in Fig. 5. The pattern of GC substrate is also shown in the lower part of Fig. 5 for the comparison. The upper pattern indicates that the deposit is composed of only Sb_2Te_3 intermetallic compound. The SEM photograph of the compound of 38 at%Sb-62%Te is shown in Fig. 6. The deposit had a relatively homogeneous surface consisting of disk-like granules with about 10 μm disk diameter.

4. Discussion

The redox of Sb(III) to Sb metal and Te(IV) to Te metal in $AlCl_3$-NaCl-KCl eutectic melt at 423 K was presented in the previous study.[6] If compared with the redox behavior, the potential for the redox couple of Sb(III)/Sb(0) in Fig. 2 is assumed to be 0.95 V vs. Al/Al(III), and the potential of Te(IV)/Te(II) and Te(II)/Te(0), 1.5 V and 1.1 V, respectively. In the anodic sweep in the Fig. 2, the dissolution of metallic Sb occurs at 1.0 V and the dissolution of Sb-Te intermetallic compound such as Sb_2Te_3 or SbTe probably occurs at 1.2 and 1.3 V. In the cathodic sweep, the purple fog was observed at potential of lower than 1.5 V. We believe that the fog is composed of an ionic species of Te.

For the electrodeposition of Sb-Te alloys under the various electrolysis potentials, the compositions of the electrodeposits were almost same; however, composition of the deposit strongly depend on the Sb (III) and Te (IV) concentration in molten salt. As seen in the voltammogram of Fig. 3, cathodic current at the potentials of 0.9 V–0.8 V increases with increase of the Sb(III) concentration in the melt. It was shown in Fig. 4, that Sb concentration in the deposition depends on the Sb (III) concentration in the melt in the potential region except for the concentration ratio of Sb(III) to (Sb (III) + Te (IV)). In the potential region, the electrodeposition may be controlled by the diffusion process in the melt. In the ratio less than 0.4, no stable deposit was not observed, as reported in the previous paper,[6] pure Te metal was hardly deposited, because it removed into the melt immediately after the dendric deposition. The Te deposit may be stabilized by co-deposition with Sb. In order to prepare Sb_2Te_3 intermetallic compound suitable for the thermoelectric device, it was found to control the concentration ratio of Sb(III) to (Sb (III) + Te (IV)) at 0.4 at the deposition potentials from 0.8 to 0.9 V.

The XRD result in Fig. 5 suggests that the compound in the deposit is composed of Sb_2Te_3 intermetallic compound with the hexagonal structure and consists of the disk-like granules surface morphology.

It is noticeable that the granules size in Fig. 6 is about 3 times larger than those of the electrodeposit from the aqueous solution system.[5]

5. Conclusions

The electrodeposition of Sb-Te alloys was successfully prepared in $AlCl_3$-NaCl-KCl molten salt containing Sb (III) and Te (IV) at 423 K.

(1) There is a linear relation between the concentration of Sb to Sb and Te in the deposit and the concentration ratio of Sb (III) to (Sb (III) + Te (IV)) in the melt, except for the ratio less than 0.4.
(2) The XRD pattern of the 38%Sb-62%Te deposit indicates that the compound is composed of Sb_2Te_3 intermetallic compound. The surface of the deposit is relatively homogeneous and consists of disk-like granules with about 10 μm diameter.

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