Preparation of Cobalt-Antimony Thermoelectric Film using Pulse Electrolysis in Ethylene Glycol-CoCl₂-SbCl₃ Non-Aqueous Solution

Hiroaki YAMAMOTO a,*, Masao MORISHITA a, Yuki KUKIMOTO b and Tomohiro HAGIO b

a Department of Chemical Engineering and Materials Science, Graduate School of Engineering, University of Hyogo(2167, Shosha, Himeji-shi, Hyogo 671-2280)
b Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo(2167, Shosha, Himeji-shi, Hyogo 671-2280)

The preparation of cobalt-antimony thermoelectric film using pulse electrolysis was investigated in ethylene glycol (EG)-CoCl₂-SbCl₃ non-aqueous solutions at 393 K. The layered structures consisting of Co rich Co-Sb alloy layers and Sb rich Co-Sb alloy layers were obtained by applying alternately the potentials for electrodepositing the former, E₁, and the latter, E₂, in the 90.0 mol%EG-9.09 mol%CoCl₂-0.91 mol%SbCl₃ bath, and were heat-treated at 673 K for 24 h in Ar gas atmosphere to prepare the Co-Sb alloy films with uniform composition. The composition of Co-Sb alloy film was found to be controlled by adjusting the ratio of applied duration at E₁, t₁, and one at E₂, t₂, in the potential rectangular wave used in the pulse electrolysis. At the (t₁ / t₂) ratio of 7.0, the Co-Sb alloy film with the composition of 26.1 mol%Co-73.9 mol%Sb was obtained after heat treatment. This alloy film was not the CoSb single phase, but included as constituent and exhibited a p-type thermoelectric conversion by the given temperature difference.

Keywords: Pulse Electrolysis, Cobalt-Antimony Alloy, Thermoelectric Material, Non-Aqueous Solution

1. Introduction

The thermoelectric materials can convert the thermal energy directly into the electrical energy and the thermoelectrical power generation using them is considered to be one of clean energy sources. An intermetallic compound in the Co-Sb binary system, CoSb₂, is a p-type semiconductor with a narrow bandgap and high hole mobility. It has a skutterudite structure and the addition of a third element to CoSb₂ significantly improves their thermoelectric properties. For example, it is reported that the addition of nickel to CoSb₂ makes its p-type thermoelectric property to n-type. Several methods such as hot pressing, vacuum melting, mechanical alloying, and physical vapor deposition have been used and studied to prepare thermoelectric materials. Because thermoelectric devices usually consist of pairs of p- and n-type semiconductors, the preparation of thermoelectric materials in film has advantage in the ability to produce lightweight and high-capacity devices. We focused on the electrodeposition method, which uses a simple apparatus and experimental procedure and is suitable for mass film production. Choosing the non-aqueous solutions, it has possibilities to obtain various kinds of metals and alloys by electrodeposition without the generation of hydrogen gas, which decreases the coulomb efficiency.

Associating with previous studies, the Zn plating and Zn-Mg alloy plating with high-corrosion resistance on the steel for automobile were investigated in non-aqueous solutions using ionic liquids such as 1-ethyl-3-methylimidazolium bromide (EMIB) and trimethyl propylammonium bis(trifluoromethyl sulfonyl) imide (TMPATFSI), and ethylene glycol (EG) based baths. We had used EG as additive in the ionic liquids for improving the coulomb efficiency and surface morphology of electrodeposits. Because it was found that a relatively large amount of metallic salts was dissolved in EG at 393 K, we conceived of an idea using EG as solvent for electrodeposition of metals and alloys. Recently, we have reported the electrodeposition of Zn-Sb and Co-Sb thermoelectric materials in the EG-based non-aqueous solutions. In the study of electrodeposition of Co-Sb alloy, the optimization of the composition for EG-CoCl₂-SbCl₃ bath and the electrolysis condition such as applied potential in potentiostatic electrolysis made it possible to control the composition of co-electrodeposited Co-Sb alloy, obtaining the conditions to electrodeposit Co-Sb alloys consisting of electrodeposited CoSb as constituent. However, it was also suggested that the conditions for obtaining the single phase of CoSb were severe and it required the constancy of EG-CoCl₂-SbCl₃ bath composition during electrolysis.

Some studies about the electrodeposition of Co-Sb thermoelectric materials in aqueous solutions have been reported, and Behnke et al. investigated the preparation of Co-Sb alloy in aqueous solutions containing cobalt sulfate, antimony (III) oxide, potassium citrate, and citric acid using a pulse electrolysis method. This pulse electrolysis method appears to be advantageous to overcome the problem mentioned above. The pulse electrolysis is a method applying different potentials alternately as a potential rectangular wave on the substrate. In the present study, the pulse electrolysis method was applied to the electrodeposition in the EG-CoCl₂-SbCl₃ non-aqueous solutions. The pulse electrolysis was used to prepare a layered structure consisting of Co-rich Co-Sb alloy layers and Sb-rich Co-Sb alloy layers and the heat treatment was used to react Co and Sb to prepare the Co-Sb alloy with uniform composition. In the present paper, the conditions of pulse electrolysis were investigated to prepare the Co-Sb alloy film with p-type thermoelectric conversion function.

* E-mail: hyama@eng.u-hyogo.ac.jp
2. Experimental

2.1 Preparation of baths

The electrolytic baths used for pulse electrolysis were composed of ethylene glycol (EG, purity: >99.5%, water content: <0.2%, Kanto Chemical Co., Inc.) and cobalt chloride (CoCl₂, purity: 99.999%, Kojundo Chemical Lab. Co., Ltd.) as the Co ion source, and antimony (III) trichloride (SbCl₃, purity: 99.9%, Kojundo Chemical Lab. Co., Ltd.) as the Sb ion source. The chemicals were weighed in the composition of 1 mol%CoCl₂, 0 mol%CoCl₂, and 0 mol%SbCl₃, where the molar ratio of CoCl₂ to SbCl₃ was 10 to 1 and the total concentration of metallic salts was 10.0 mol%. The mixture was dehydrated at 343 K for 24 h under vacuum using a rotary pump to prepare the electrolytic baths. The dehydrated mixture was heated up to 393 K for experimental use.

2.2 Pulse electrolysis and heat treatment

In the electrolysis and electrochemical measurements, a copper sheet (purity: 99.96%, 0.3 mm × 30 mm × 10 mm, Nilaco Co.) electropolished in orthophosphoric acid, and a cobalt sheet (purity: 99.9%, 0.3 mm × 30 mm × 10 mm, Nilaco Co.) degreased with acetone were used as the cathode and the anode, respectively. A reference electrode used in the present study was a Zn wire immersed in a separated fritted glass tube containing the 85.0 mol%EG-15.0 mol%ZnCl₂ bath. All potentials concerning about the electrochemical experiments in the present paper were referenced to this electrode.

Before the pulse electrolysis, the cathodic polarization curves were measured to study the reduction behavior of Co and Sb species in the EG based baths. The electrodes mentioned above were immersed in the bath and were connected to the automatic polarization system (HSV-110, HOKUTO DENKO Corp.) and the potential was swept from the rest potential to negative at a scan rate of 0.05 V s⁻¹ to measure the cathodic polarization curves.

On the basis of the reduction potentials of Co and Sb species, the potentiostatic electrolyses were conducted in the potential range from 0.5 V to −1.0 V in the 90.0 mol%EG-9.1 mol%CoCl₂-0.9 mol%SbCl₃ bath at 393 K for 2.5 × 10³ C cm⁻² to clarify the relationship between such potentials and the compositions of electrodeposits.

The pulse electrolysis was used for the preparation of the layered structure consisting of two kinds of alloys having different composition and was conducted by the potentiostat (HAL-3001, HOKUTO DENKO Corp.) using a potential rectangular wave generated by the function generator (HB-305, HOKUTO DENKO Corp.). Fig. 1 shows the schematic diagram of potential rectangular wave for the pulse electrolysis. The potentials for electrodeposition the Co rich Co-Sb alloy and the Sb rich Co-Sb alloy are E₁ and E₂, respectively, determined from the results of potentiostatic electrolysis mentioned above. The durations for electrodeposition at the potentials of E₁ and E₂ in a period of potential rectangular wave are indicated as t₁ and t₂, respectively. The pulse electrolysis was carried out at various (t₂ / t₁) ratio in the 90.0 mol%EG-9.1 mol%CoCl₂-0.9 mol%SbCl₃ bath at 393 K for 2.5 × 10³ C cm⁻² using the copper cathode and the cobalt anode. After the electrolysis, the electrodeposited was heat treated at 673 K for 24 h in Ar gas atmosphere to prepare the Co-Sb alloy with uniform composition.

The structural characterization and the quantitative analysis for the surface of the film were performed by X-ray diffractometer (RINT-2200, Rigaku Corp.) and electron probe microanalyzer (EPMA, JXA-8900R, JEOL Ltd.).

The preparation of bath and the electrolysis were carried out in an Ar-gas-filled glove box (DB-1-W, MIWA MFG).

2.3 Measurement of thermoelectric force

The thermoelectric conversion test of the Co-Sb alloy film was performed by measuring the thermoelectric force that was generated by given temperature difference at room temperature. The temperature difference was developed by heating the electrodeposited end and radiating the other end (non-electrodeposited end) of the Cu substrate. The temperatures at the two points (low temperature point: 300 ± 2 K, high temperature point: 302-310 K) are the temperature difference developed by heating the electrodeposited and the generated thermoelectric force was measured by using a digital multimeter (R6552, Advantest Corp.).

3. Results and Discussion

3.1 Determination of condition for pulse electrolysis

The reduction behavior of the Co and Sb species in EG-CoCl₂-SbCl₃ baths were investigated by measuring the cathodic polarization curves. Fig. 2 shows the cathodic polarization curves measured at a scan rate of 0.05 V s⁻¹ in the following baths: Bath A, 90.0 mol%EG-9.1 mol%CoCl₂-0.9 mol%SbCl₃; Bath B, 99.0 mol%EG-1.0 mol%SbCl₃; Bath C, 90.0 mol%EG-10.0 mol%CoCl₂.
polarization curves measured in the following baths: Bath A, 90.0 mol%EG-9.1 mol%CoCl₂-0.9 mol%SbCl₃; Bath B, 99.0 mol%EG-1.0 mol% SbCl₃; Bath C, 90.0 mol%EG-10.0 mol%CoCl₂. In Bath A, the cathodic current was observed initially at 0.75 V and its increase was once limited at 0.30 V followed by the re-increase at 0.25 V. On the other hand, the initial increases in cathodic currents were observed at 0.75 V in Bath B and 0.25 V in Bath C, and these were obviously caused by the reductions of Sb ionic species to Sb and Co ionic species to Co, respectively. This suggested that the increase in current density observed at 0.75 V and 0.25 V in Bath A were mainly caused by the reduction of Sb ionic species to Sb and the increase in the amount of co-electrodeposited Co with Sb, respectively. The cathodic current measured in Bath A was larger than the summation of those for Bath B and Bath C. As described below in Fig. 3, the co-electrodeposition of Co was observed at the potentials lower than 0.25 V (under potential deposition). Furthermore, the interaction between Co and Sb ionic species in Bath A may cause the change in ratio of these ionic species. It is presumed that these are the reasons for the large cathodic current density observed in Bath A.

The relationship between the applied potential and the Co content in electrodeposition obtained by potentiostatic electrolysis in Bath A had been already reported in our previous paper. However, it was re-investigated in wider potential range to find the suitable potentials for pulse electrolysis ($E_{co}$ and $E_{so}$ in Fig. 1).

Fig. 3 shows the Co content in electrodeposits obtained by the potentiostatic electrolysis in Bath A. The Co content in electrodeposits increased with the applied potential and it exhibited significant increase at around 0.25 V. This potential coincided well with the potential corresponding to the increase in amount of Co co-electrodeposited as observed in the cathodic polarization curve measured in Bath A as shown in Fig. 2. Because the Co content of CoSb, which is the thermoelectric material in Co-Sb system, is 25 mol% and the slight fluctuation of electrolysis conditions such as potential, current density, and bath composition violates the stoichiometry of CoSb, it requires the strict control of applied potential in constant bath composition during electrolysis to obtained CoSb single phase by using potentiostatic electrolysis in Bath A. In Fig. 3, the compositions of electrodeposits obtained at lower potential than −0.4 V were almost the same independent of the applied potential and 68.2 mol%Co−31.8 mol%Sb alloy was obtained at −0.6 V. In the same way, the compositions of electrodeposits obtained at higher potential than 0.3 V were almost the same and 0.3 mol%Co−99.7 mol%Sb alloy was obtained at 0.4 V. From this result, $E_{co}$ and $E_{so}$ were determined to −0.6 V and 0.4 V, respectively. Average current densities, compositions of electrodeposits, and deposition rates of Co and Sb calculated by the Faraday's law at the potentials of −0.6 and 0.4 V during the potentiostatic electrolysis were summarized in Table 1. These calculated deposition rates suggested that $E_{so}$ should be longer than $E_{co}$ in order to obtain the specimen having the composition of CoSb.

![Fig. 3](image-url) Co content in the electrodeposits obtained by potentiostatic electrolysis in the 90.0 mol%EG-9.1 mol%CoCl₂-0.9 mol%SbCl₃ bath for 2.5 × 10² Cm⁻² at 393 K.

![Fig. 4](image-url) X-ray diffraction patterns of the electrodeposits obtained at the potentials of (a) −0.6 V and (b) 0.4 V in the 90.0 mol%EG-9.1 mol%CoCl₂-0.9 mol%SbCl₃ bath for 2.5 × 10² Cm⁻² at 393 K.

### Table 1

| Potential, $E/V$ | Current density, $i/Am^{-²}$ | Composition of electrodepos | Deposition rate /mmol s⁻¹ m⁻² |
|-----------------|-----------------------------|----------------------------|--------------------------------|
| −0.6            | −482                        | 68.2 mol%Co−31.8 mol%Sb    | Co : 1.47                        |
|                 |                             |                            | Sb : 0.685                        |
| 0.4             | −122                       | 0.3 mol%Co−99.7 mol%Sb     | Co : 1.27 × 10⁻²                   |
|                 |                             |                            | Sb : 0.421                        |

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Co-Sb film shown in Fig. 3. In the X-ray diffraction pattern of 68.2 mol%Co-31.8 mol%Sb alloy film as shown in Fig. 4(a), an indistinct and broadened peak of Co was detected at around 44 degrees of 2θ and this peak was shifted to the lower degree compared with pure Co. On the basis of the phase diagram of the Co-Sb binary system, little amount of Sb dissolves in Co. Therefore, a portion of Sb in electrodeposit formed Cu₅Sb with the Cu substrate and the remaining Sb formed the supersaturated solid solution with Co in nonequilibrium state. In the X-ray diffraction pattern of 0.3 mol%Co-99.7 mol%Sb alloy film as shown in Fig. 4(b), the X-ray diffraction peaks of Sb were mainly detected.

Fig. 5 shows the SEM images for the surface of electrodeposits obtained at (a) 0.6 V and (b) 0.4 V. As shown in Fig. 5(a), the rounded particles were observed on the surface of electrodeposits obtained at 0.6 V. On the other hand, the crystals reflecting the rhombohedral structure of antimony were observed on the surface of electrodeposits obtained at 0.4 V as shown in Fig. 5(b).

3.2 Preparation of Co-Sb alloy film using pulse electrolysis and heat treatment

Pulse electrolyses were conducted in the 90.0 mol%EG-9.1 mol%CoCl₂-0.9 mol%SbCl₃ bath by using the determined $E_{co}$ (−0.6 V) and $E_{co}(0.4 V)$ for the potential rectangular wave. The change in cathodic reaction caused by the potential rectangular was investigated by measuring the cathodic current during the pulse electrolysis. Fig. 6 shows the cathodic current density during the pulse electrolysis under the $(t_{sa} / t_{co})$ ratio of 7.0, where $t_{co}$ was 2.0 s and $t_{sa}$ was 14 s. Although the spike currents were observed just after the changeover of potential, it was confirmed that the change in cathodic current showed the rectangular wave according to the change in applied potential. In addition, the averages of plateau current densities corresponding to the applied potentials of −0.6 and 0.4 V in Fig. 6 were about 475 and −105 Am⁻², respectively, correlated with the average current densities measured during the potentiostatic electrolyses shown in Table 1. These suggested that almost the same alloys as obtained by the potentiostatic electrolyses at −0.6 and 0.4 V were electrodeposited alternately in the pulse electrolysis. The homogeneous heat treatments of the layered structures obtained by the pulse electrolyses were attempted by holding them at 673 K for 24 h in Ar gas atmosphere.

Fig. 7 shows the Co content in specimens after heat treatment for the pulse-electrodeposits obtained by varying $(t_{sa} / t_{co})$ ratio. A dashed line in Fig. 7 shows the estimated Co content of specimen calculated from the amount of Co and Sb obtained by multiplying the durations for electrodeposition in a period of potential reta-
gular wave ($t_{ca}$ and $t_{ce}$) and the average deposition rates of Co and Sb at -0.6 and 0.4 V shown in Table 1 on the assumption that the compositions of electrodeposits obtained at -0.6 and 0.4 V in the pulse electrolyses were the same as those of electrodeposits obtained by potentiostatic electrolyses at -0.6 and 0.4 V, and the Co rich alloy and Sb rich alloy were electrodeposited alternately with 100% of the cathodic current efficiencies. As expected from the estimated value, the experimental Co content in specimen decreased with ($t_{ca}$ / $t_{ce}$) ratio and its change was almost the same as estimated value. Strictly speaking, there were small discrepancies between the experimental and the estimated Co content. The spike currents were observed with every changeover of applied potential as shown in Fig. 6. The spike current resulted from charging the electricity to the electric double layer on the cathode does not contribute to electrodeposition of Co and Sb, meaning that such a transition state decreases the duration of the electrodeposition. Furthermore, it could not be denied that the anodic dissolution of Co at 0.4 V, especially under the condition of high ($t_{ca}$ / $t_{ce}$) ratio. Counterbalancing these factors, the discrepancy between the experimental and estimated Co content in Fig. 7 were caused. The composition of the alloy film obtained at the ($t_{ca}$ / $t_{ce}$) ratio of 7.0 was 26.1 mol%Co-73.9 mol%Sb, that is, it was the closest to the composition of CoSb$_3$ in the present study. Fig. 8 shows the X-ray diffraction patterns of this specimen (a) before and (b) after heat treatment at 673 K for 24 h in Ar gas atmosphere. As shown in Fig. 8(a), X-ray diffraction peaks of Sb were detected and that of Co was not detected in the electrodeposited before heat treatment. The conditions of pulse electrolysis, charge was the closest to the composition of CoSb$_3$ and/or Co and Sb that did not react enough in the heat treatment may exist in the specimen. As can be seen from Fig. 7, the Co content of specimen changes gently with the ($t_{ca}$ / $t_{ce}$) ratio, which is an important parameter for controlling the composition of Co-Sb alloy in the pulse electrolysis and it is easy to set up by using a function generator to apply the potential rectangular wave. Therefore, in order to control the composition of Co-Sb alloy prepared from EG-CoCl$_2$-SbCl$_3$ bath, the pulse electrolysis method using in this study is better than the potentiostatic electrolysis conducted in a proper bath composition using a strict potential.

3.3 Thermoelectric effect of the electrodeposition

The thermoelectric effect of the 26.1 mol%Co-73.9 mol%Sb alloy film with a thickness of approximately 5 μm on the Cu substrate was confirmed at room temperature. Fig. 9 shows the thermoelectric force generated by the given temperature difference. The thermoelectric force was observed to increase with the temperature difference. The apparent Seebeck coefficient of this specimen, which was calculated by the slope of the solid line in Fig. 9, was approximately 55 μVK$^{-1}$. As a result of the positive Seebeck coefficient, this alloy film was confirmed to be a p-type thermoelectric material.

Fig. 10 shows the relationship between Co content and Seebeck coefficient of Co-Sb alloy films. An open circle symbol indicates the Seebeck coefficient of 26.1 mol%Co-73.9 mol%Sb alloy film obtained by using the pulse electrolysis in the present study and the others show that of Co-Sb alloy films obtained by using potentiostatic and galvanostatic electrolysis in our previous studies$^{21}$. It can be seen that the Seebeck coefficient of Co-Sb alloy film increases as its Co content comes close to 25.0 mol% that is the stoichiometric composition of CoSb$_3$. This suggests that the
composition control is important to improve the Seebeck coefficient of Co-Sb alloy film and the pulse electrolysis method used in this study is more useful for the composition control than the potentiostatic and galvanostatic electrolysis method.

4. Conclusions

The preparation of Co-Sb thermoelectric film was investigated by using the method combining the pulse electrolysis in ethylene glycol (EG)-CoCl₂-SbCl₃, non-aqueous solutions and the heat treatment. The pulse electrolysis method was used to prepare a layered electrodeposited-structure consisting of Co rich Co-Sb alloy layers and Sb rich Co-Sb alloy layers, applying alternately the potentials for electrodepositing the former, E_co, and the latter, E_sb, in the 90.0 mol%EG-9.09 mol%CoCl₂-0.91 mol%SbCl₃ bath at 393 K. Adjusting the ratio of applied duration at E_co, t_co, to one at E_ssb, t_ssb, in the potential rectangular wave used in the pulse electrolysis, the 26.1 mol%Co-73.9 mol%Sb alloy film consisting of CoSb, as constituent was obtained at the t_co / t_ssb ratio of 7.0, followed by the heat treatment at 673 K for 24 h in Ar gas atmosphere, and this alloy film exhibited a p-type thermoelectric conversion by the given temperature difference. Since the potential rectangular wave can be easily applied by the function generator and potentiostat, the composition control of Co-Sb alloy using the pulse electrolysis is easier, compared to the coelectrodeposition method.

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