Electrodeposition of Nb₅Sn Alloy Film from Lewis Basic NbCl₅-SnCl₂-EMIC Melt

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The electrodeposition of the Nb₅Sn alloy film from the Lewis basic NbCl₅-SnCl₂-EMIC melt (50 mol% < EMIC) was investigated. The relationship between melting point or glass transition point and molar fraction of NbCl₅ was constructed for the NbCl₅-EMIC system, which showed a melting point less than room temperature in the range of 10.0 mol% ≤ molar fraction of NbCl₅ ≤ 33.3 mol%. From the results of the cyclic voltammograms, the possibility of electrodeposition of the Nb₅Sn alloy film was suggested from the Lewis basic melt. The Nb₅Sn alloy film was reproducibly obtained from the 19.2 mol% NbCl₅–10.0 mol% SnCl₂–70.8 mol% EMIC bath using a constant current pulse electrodeposition method at 0.1 A cm⁻² with a pulse period of 10 ms, duty ratio of 0.20, and electricity of 50 C cm⁻² at 130 °C, although the existence of the metallic Sn simple substance and the Cu-Sn alloy in the film was confirmed by an XRD analysis.

Key Words : Electrodeposition, Nb₅Sn Alloy, Ambient-temperature Molten Salt, 1-Ethyl-3-methylimidazolium Chloride

1 Introduction

The Nb₅Sn alloy is one of the commercially used superconductor materials. It is used as a superconducting magnet in a magnetic resonance imaging (MRI) device for medical examinations and expected to be used in a nuclear fusion reactor. However, it is very difficult to make the Nb₅Sn alloy into linear shapes, because it is an intermetallic compound and very brittle. Therefore, its fabrication process requires many steps. In contrast, it is possible to make the electrodeposited material into various shapes in one step if an electrodeposition method is applied. Our group reported that various kinds of alloys could be electrodeposited from 1-ethyl-3-methylimidazolium chloride (EMIC) based ambient-temperature molten salt melts.10 It was found that it was possible to electrodeposited the Nb₅Sn superconductor alloy film from a Lewis acidic melt (EMIC < 50 mol%), i.e., 68.6 mol% NbCl₅–28.6 mol% SnCl₂–28.6 mol% EMIC melt, using a constant current electrodeposition method.20 The Tc (onset) and Tc (zero) of the obtained electrodeposited alloy by resistivity measurements using a DC four-lead method were 19 K and 16 K, respectively. However, it is hard to get reproducible alloy film compositions, and the optimal conditions for the electrode fabrication have not yet been determined. In this study, we investigated the electrodeposition condition that influence the composition of the alloy film using a Lewis basic melt (50 mol% < EMIC) in order to further improve the reproducibility of the electrodeposited film consisting of Nb₅Sn alloy.

2 Experimental

The EMIC was synthesized as previously reported.10 The SnCl₂-EMIC melt was prepared at the desired molar ratio by mixing EMIC with SnCl₂ (Wako Pure Chemical Industries, Ltd., 99.9%) at 130 °C. A small quantity of NbCl₅ (Soekawa Chemical Co., Ltd., 99.9%) was then slowly added to the melt. The electrodeposition bath was then obtained after it was left for 24 h at 130 °C. The melting point and the glass transition point were measured by means of a differential scanning calorimeter DSC-60 (Shimadzu Co., Ltd.).

The cyclic voltammetry (CV) and electrodeposition processes were carried out using a three-electrode cell. The former cell consisted of the Al (III)/Al reference electrode, a W wire (Nilaco, 99.95%, φ 1 mm) (W.E.), and a Sn plate (99.9%) (C.E.). The latter cell consisted of a W wire (Nilaco, 99.95%, φ 1 mm) as a quasi-reference electrode, a Cu plate (99.96%, 1.0 cm²) cathode, and a Sn plate (99.9%) anode. The electrochemical experiments were performed using a computer-controlled electrochemical measuring system (Hokuto Denko, HZ-3000) for the CV measurement. The constant current electrodeposition was carried out using a current pulse generator (Nikkol Keiso, NCG-10-10). The crystal structure of the electrodeposited films was examined by X-ray diffraction (XRD) using an X-ray diffractometer (Rigaku Denki, RAD-C, 40 kV, 25 mA) with Cu-Kα radiation (λ = 0.15418 nm).

The melt preparation and the electrochemical measurements were carried out in a glove-box with an Ar atmosphere (MIWA MFG Co., Ltd., 1ADB-3LL)
3 Results and Discussion

Figure 1 shows the relationship between melting point or glass transition point and molar fraction of NbCl$_5$ determined by the DSC measurements. It was found that the glass transition point were less than $-40^\circ$C in the range of 10.0 mol%$\leq$ molar fraction of NbCl$_5 \leq$ 33.3 mol% and the melting point showed more than 40 $^\circ$C in the range of 40.0 mol%$\leq$ molar fraction of NbCl$_5 \leq$ 60.0 mol%. Based on the result, the Lewis basic melt in the above range, which was liquid at room temperature, was evaluated as an electrodiposition bath.

The CV of the 4.4 mol% SnCl$_2$-95.6 mol% EMIC melt was measured at 130 $^\circ$C and 10 mV s$^{-1}$ in order to investigate the electrochemical redox behavior of the Lewis basic SnCl$_2$-EMIC melt (Fig. 2). The reduction wave and the oxidation wave corresponding to the deposition and dissolution reactions of Sn were clearly observed in the potential range from $ca.$ -1.07 to $ca.$ -1.30 V vs. Al (III)/Al and from $ca.$ -1.05 to $ca.$ -0.75 V vs. Al (III)/Al, respectively.

As for the CV of the 33.3 mol% SnCl$_2$-66.7 mol% BPC (1-butlypyridinium chloride) melt, the coupled redox peak clearly appeared at about -0.7 V vs. Sn (II)/Sn. This redox reaction was considered according to the following equation (1) $^6$:

$$\text{SnCl}_2^- + 2e^- \rightarrow \text{Sn} + 3\text{Cl}^-$$

(1)

Moreover, it was clarified that the SnCl$_2^-$ - EMI$^+$ complex existed in the 33.3 mol% SnCl$_2$-66.7 mol% EMIC melt.$^7$ It was suggested that this coupled redox peak would be the deposition and dissolution of Sn according to equation (1) because the main Sn anionic species was SnCl$_2^-$ in the Lewis basic melt.

The CV of the 11.9 mol% NbCl$_5$-88.1 mol% EMIC melt was measured at 130 $^\circ$C and 10 mV s$^{-1}$ in order to investigate the electrochemical redox behavior of the Lewis basic NbCl$_5$-EMIC melt (Fig. 3). The reduction waves from $ca.$ 0.21 V vs. Al(III)/Al and $ca.$ -0.77 V vs. Al (III)/Al were observed. The CV’s profile of this melt was similar to that of the 49.0 mol% AlCl$_3$-51.0 mol% EMIC melt containing the [NbCl$_6$]$^{3-}$ ion.$^8$ Sun et al. reported the reaction equations regarding the niobium anionic species according to equations (2) and (3).

$$[\text{NbCl}_6]^{3-} + e^- \rightarrow [\text{NbCl}_5]^{2-}$$

(2)

$$[\text{NbCl}_5]^{2-} + e^- \rightarrow [\text{NbCl}_6]^{3-}$$

(3)

In this case, the peak potentials of the two reduction waves corresponding to Nb(V)/Nb(IV) and Nb(IV)/Nb (III) were approximately 0.153 V vs. Al(III)/Al and -0.958 V vs. Al(III)/Al, respectively. On the other hand, we reported that the main niobium anionic species was the [NbCl$_6$]$^{3-}$ ion and the NbCl$_5^-$ - EMI$^+$ complex existed in the 33.3 mol% NbCl$_5$-66.7 mol% EMIC melt.$^9$ Based on these results, it was suggested that the two reduction waves in Fig. 3 would be the reduction reactions of the niobium anionic species corresponding to Nb(V)/Nb(IV) and Nb(IV)/Nb(III), respectively.
Fig. 4 Cyclic voltammogram of the 19.2 mol\% NbCl$_5$–10.0 mol\% SnCl$_2$–70.8 mol\% EMIC melt (130 °C). Scan rate: 10 mV s$^{-1}$.

Fig. 5 XRD pattern of the electrodeposited from the 19.2 mol\% NbCl$_5$–10.0 mol\% SnCl$_2$–70.8 mol\% EMIC bath. ○: Nb$_2$Sn, ■: Sn, ▲: Cu$_2$Sn$_3$, ⊘: Cu (sub). Bath temperature: 130 °C, current density: 0.1 A cm$^{-2}$, pulse period: 10 ms, duty ratio: 0.20, and electricity: 50 C cm$^{-2}$.

The CV of the 19.2 mol\% NbCl$_5$–10.0 mol\% SnCl$_2$–70.8 mol\% EMIC melt was measured at 130 °C and 10 mV s$^{-1}$ in order to investigate the electrochemical redox behavior of the Lewis basic NbCl$_5$-SnCl$_2$-EMIC melt (Fig. 4). Two reduction waves were observed at the potential that was lower than $-0.5$ V vs. Al (III)/Al. Compared with Figs. 2 and 3, it was considered that the reduction wave was the reduction reaction of the niobium anionic species from ca. $-0.5$ V vs. Al (III)/Al and the another reduction wave was that of the tin anionic species from ca. $-0.8$ V vs. Al (III)/Al, indicating that the codeposition reaction of Nb and Sn might occur because both reduction potentials were very close to each other.

The electrodeposition from the 19.2 mol\% NbCl$_5$–10.0 mol\% SnCl$_2$–70.8 mol\% EMIC bath was attempted using a constant current pulse electrodeposition method at 0.1 A cm$^{-2}$ with a pulse period of 10 ms, duty ratio of 0.20, and electricity of 50 C cm$^{-2}$ at 130 °C. The surface of the electrodeposits was crack-free and the morphology was almost homogeneous (not shown). Figure 5 shows the XRD pattern of the electrodeposits. The peaks at 37° and 41° indexed to the Nb$_2$Sn alloy were observed. However, the peaks assigned to metallic Sn and the Cu-Sn alloy were also detected. As for the formation of the Cu-Sn alloy, it was reported that the Cu-Sn layer grew due to the solid-phase interdiffusion of the Cu and Sn atoms when Sn was electrodeposited on the Cu substance over 100 °C. Therefore, it was considered that Cu$_2$Sn$_3$ would be formed because the Sn simple substance, which was electrodeposited at 130 °C, had mutually diffused with the Cu substance. Additionally, the Lewis basic NbCl$_5$-SnCl$_2$-EMIC melt was more volatile than the Lewis acidic melt at ca. 130 °C and it was thermally more stable.

Therefore, it was judged that the Lewis basic melt would be comparatively suitable as an electrodeposition bath.

4 Conclusion

In this study, we attempted the electrodeposition of the Nb-Sn alloy film using the Lewis basic melt having a low melting point. The Nb-Sn alloy film was reproducibly obtained from the 19.2 mol\% NbCl$_5$–10.0 mol\% SnCl$_2$–70.8 mol\% EMIC bath using a constant current pulse electrodeposition method at 0.1 A cm$^{-2}$ with a pulse period of 10 ms, duty ratio of 0.20, and electricity of 50 C cm$^{-2}$ at 130 °C, although the metallic Sn simple substance was codeposited and Cu$_2$Sn$_3$ was formed in the film. The next step would be to prevent the metallic Sn simple substance from depositing not to form Cu-Sn alloy in the film.

References