ELECTRODEPOSITION AND DISSOLUTION OF Nb AND Al IN MOLTEN CHLORIDE BATHS

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ABSTRACT

Since Nb₃Al is a promising superconductor material, electrodeposition of Al-Nb alloys was attempted in LiCl-KCl and AlCl₃-NaCl melts containing niobium and aluminum ions. The electrochemical behavior of these ions was studied by using cyclic voltammetry and potentiostatic electrolysis on niobium and aluminum electrodes at 473K(AlCl₃-NaCl) and 773K(LiCl-KCl) respectively. Electrodeposition was carried out in baths in which niobium ion was produced by anodic dissolution of the metal. A small amount of deposit was obtained and was found to be Nb from LiCl-KCl melt. On the other hand, a black deposit was obtained from an AlCl₃-NaCl melt containing Nb ion. The deposit in this case was found to be an Al-Nb alloy.

INTRODUCTION

The intermetallic compound Nb₃Al is expected to be a viable a superconductor in the near future because of its high critical temperature and high critical current density. Electrodeposition can be used to produce a variable composition of the alloy by selecting conditions of the electrolysis.

In this case, molten salts are appropriate to the electrodeposition because both aluminum and niobium are electrochemically active. There are many studies about the electrochemistry of niobium ion in molten salts.(1-6) Many studies have also been reported about the electrodeposition of Al from molten salts, especially the electrodeposition of Al-Mn alloy for industrial applications.(7)

In this work, the electrochemical behavior of aluminum and niobium ions was investigated by using LiCl-KCl and AlCl₃-NaCl melts containing niobium and aluminum ions. The methods used are cyclic voltammetry and potentiostatic electrolysis. The deposits
obtained were evaluated by SEM and EPMA (Shimadzu EPMA-8705). The purpose of this study is to clarify the electrochemical behavior of Nb and Al.

EXPERIMENTAL

In this work, LiCl-40mol%KCl eutectic and AlCl₃-48mol%NaCl melts were used as the electrolytes.

In the authors, previous work, NbCl₅, Nb₃Cl₈ and anodically dissolved Nb were used as the niobium source in AlCl₃-48mol%NaCl electrolyte. The highest content of Nb, about 80wt%, was found for the anodically dissolved Nb at 473K (8).

Therefore niobium ion was produced by anodic dissolution of metallic niobium electrodes to study the behavior of Nb species in the melt.

LiCl-KCl Bath

The electrolyte used was 60mol%LiCl-40mol%KCl eutectic melt and the working temperature was 773K.

The cell design is shown in Fig. 1. The cell was made of Pyrex glass. A reference electrode, a counter electrode, a working electrode and a thermocouple were immersed into the melt. The cell atmosphere was dry argon and the melt was stirred by bubbling argon through it.

Electrodes used are shown in Fig. 2. Niobium wire (diameter 0.5mm) or aluminum (diameter 0.9mm) was used as the working electrode. A tungsten plate with large surface area (1.35cm²) was used as the cathode to obtain larger amount of deposit. It was immersed in the bath to a depth of 8mm. The reference electrode was a Ag/AgCl electrode. For cyclic voltammetry, a graphite rod was used as the counter electrode. A niobium wire spiral was used for anodic dissolution.

After the electrolysis, the surface of working electrode was observed by SEM, and the composition of the deposit was determined by EPMA.

AlCl₃-NaCl Bath

The electrolyte used was 52mol%AlCl₃-48mol%NaCl melt. The melt is also the aluminum source.

The cell design was shown in previous work (8). The cell also has a reference electrode,
a counter electrode, a working electrode and a thermocouple. The reference electrode was a Al/AlCl₃(55mol%AlCl₃-45mol%NaCl) electrode. In this case, the whole cell was put into the furnace to keep the temperature of the cell constant because AlCl₃ is volatile and condenses at the cool position of the cell. Then the temperature of the cell was maintained at 473K by using both the furnace and a hot plate stirrer.

After the electrolysis, the surface of the working electrode was observed by SEM and the composition of the deposit was analyzed by EPMA.

RESULTS AND DISCUSSION

LiCl-KCl Bath

Figure 3 shows the cyclic voltammogram for an Al electrode in LiCl-KCl eutectic melt. When potential was swept from open-circuit potential in the anodic direction, a broad anodic peak appeared at about -0.5V (vs. Ag/AgCl). After the peak, anodic current increased owing to the evolution of chlorine. The peak at -0.5 V (vs. Ag/AgCl) is considered to be the dissolution potential of aluminum.

Figure 4 shows the cyclic voltammogram for niobium electrode in LiCl-KCl eutectic melt. An anodic peak was observed at about +0.5V independent of the sweep rate. The process at +0.5V is probably corresponds to the anodic dissolution of niobium. Therefore, an attempt was made to produce niobium ion by electrolysis at +0.5V.

After the electrodissolution of niobium, an electrodeposition was carried out at -0.5V at the tungsten cathode.

After electrodeposition, the surface of tungsten cathode was washed with water and analyzed by using SEM and EPMA. The SEM image of the cathode is shown in Fig. 5. The surface of the deposit was not very flat, although small deposit was observed. The concentration map of the deposit on the tungsten cathode obtained by EPMA is shown in Fig. 6. It was analyzed along the line in the figure. The deposit was found to be niobium.

AlCl₃-NaCl Bath

Figure 7 shows cyclic voltammograms at Al electrode for various sweep rates. A cathodic peak appeared at -0.1V and anodic dissolution peak was found at +0.1V. The same cathodic potential was also obtained for the tungsten electrode.

Cyclic voltammetry was carried out at a niobium electrode to understand the electrochemical behavior of niobium ion in the electrolyte.
Figure 8 shows the cyclic voltammogram obtained at a niobium electrode. Three anodic peaks appeared when the potential was swept in the anodic direction. The anodic current increased rapidly when the potential was swept to a higher anodic potential than +1.4V probably due to chlorine evolution. As niobium has many valence states, disproportionation reactions occur easily; therefore the three peaks are considered to correspond to niobium species of different oxidation potentials. The addition of niobium ion into the bath was tried by anodic dissolution based on above result. The potentials tried for the anodic dissolution of niobium were +1.0, +1.25, +1.35V, which corresponded to the three peaks in Fig. 8. However almost no current was observed and the melt was still transparent with no color. This phenomenon looks like passivation probably due to the low temperature. Then the potential was increased up to 1.4V and the anodic current was observed. The electrodeposition was tried after anodic dissolution.

The potential tried for the deposition was decided to -0.2V, which was lower than the potential of aluminum deposition, because no deposit was found at the potentials higher than 0V. Total charge used for this electrolysis was 640C.

After the electrolysis, the tungsten electrode was washed by water and analyzed by SEM and EPMA. Figure 9 shows the SEM image of the surface of the electrode. A fine deposit was observed. Figure 10 shows the concentration map of the deposit obtained by EPMA. The analysis were done along the lines in the figure. Both aluminum and niobium were found at the same points. The deposit was confirmed to be Al-Nb alloy. It was estimated the composition of the deposit to be about Al-14wt%Nb based on the intensity analysis.

CONCLUSION

Electrochemical dissolution and deposition of Al and Nb in the LiCl-KCl eutectic and 52mol%AlCl3-NaCl melts were studied. The results obtained are summarized as following section.

LiCl-KCl Bath

A broad anodic peak appeared at about +0.5V(vs. Ag/AgCl) in the cyclic voltammogram at a niobium electrode. For the aluminum electrode, the dissolution potential was approximately -0.5V. A small amount of niobium was obtained on a tungsten electrode by potentiostatic electrolysis at -0.5V from a bath in which niobium had been produced.
by anodic dissolution at +0.5V.

**AlCl$_3$-NaCl Bath**

Three anodic peaks were observed at +1.0, +1.25 and +1.35V (vs. Al/AlCl$_3$) in cyclic voltammogram at a niobium electrode. It is considered that niobium dissolves to produce niobium species of three different oxidation states in the melt. At potentials less than 0V, cathodic current is observed, and a fine deposit was obtained on the tungsten electrode after the electrolysis at -0.2V (vs. Al/AlCl$_3$). The deposit was confirmed to be Al-Nb alloy. It was estimated that the composition was Al-14wt%Nb based on the intensity analysis.

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Fig. 1  Schematic diagram of the apparatus for electro-chemical measurement for LiCl-KCl eutectic melt.

Fig. 2  Schematic diagram of the electrodes for LiCl-KCl eutectic melt.
Fig. 3 Cyclic voltammogram for aluminium electrode in LiCl-KCl eutectic melt.

Fig. 4 Cyclic voltammogram for niobium electrode in LiCl-KCl eutectic melt.
Fig. 5 SEM photograph of Nb deposited on to tungsten electrode.

Electrolyte : LiCl-KCl (Nb dissolved)
Potential : -0.5V(vs. Ag/AgCl)

Fig. 6 Concentration map of deposit on tungsten electrode after electrolysis.
Temp. : 473K
Electrolyte : LiCl-KCl (Nb dissolved at +0.5V)
Working : Tungsten cathode
Potential : -0.5V(vs. Ag/AgCl)
Fig. 7  Cyclic voltammogram for aluminium electrode in AlCl$_3$-NaCl melt.

Fig. 8  Cyclic voltammogram for niobium electrode in AlCl$_3$-NaCl melt.
Fig. 9  SEM photograph of Al-Nb deposited on tungsten electrode.

Electrolyte: AlCl$_3$-NaCl (Nb dissolved)
Potential: -0.2V (vs. Al/AlCl$_3$)

Fig. 10  Concentration map of Al-Nb alloy obtained from the AlCl$_3$-NaCl melt.

Temp.: 473K
Electrolyte: AlCl$_3$-NaCl (Nb dissolved at +1.4V)
Working: Tungsten electrode