

Electrochemical Formation of RE-Cu (RE=Dy, Nd)  
Alloys in a Molten LiCl-KCl System

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### Introduction

We proposed a new separation and recovery process for RE metals from Nd magnet scraps using molten salt electrolysis and an alloy diaphragm [1-3]. The new separation and recovery process for RE metals was first applied to chloride melts [1, 4], and the present study focused on the electrochemical formation of RE-Cu (RE=Dy, Nd) alloys in a molten LiCl-KCl system at 723 K. The separation of Dy was also investigated using a Cu electrode in a molten LiCl-KCl-DyCl<sub>3</sub>-NdCl<sub>3</sub> system.

### Experimental

All experiments were performed in LiCl-KCl eutectic melts under dry argon atmosphere at 723 K. NdCl<sub>3</sub> or DyCl<sub>3</sub> was added directly to these melts. The working electrodes were Mo (5 mm × φ 1 mm) and Cu (5 mm × φ 1 mm) wires for the investigation of electrochemical behavior. Rectangular shaped plates of Cu (20 mm × 5 mm × 0.2 mm) were used as the working electrodes. The reference electrode was a Ag<sup>+</sup>/Ag electrode. All the potentials given hereafter were referred to Li<sup>+</sup> / Li electrode potential on a Mo wire. The counter electrode was a glassy carbon rod (50 mm × φ 5 mm). The alloy samples were prepared by potentiostatic electrolysis. After the electrolysis, the samples were analyzed by XRD, SEM and ICP-AES.

### Results and discussion

Open-circuit potentiometry was carried out with a Cu electrode after depositing Dy metal by potentiostatic electrolysis at 0.40 V (vs. Li<sup>+</sup> / Li) for 120 s in a molten LiCl-KCl-DyCl<sub>3</sub>(0.50 mol%) system at 723 K. There were four potential plateaus at (a) 0.50 V, (b) 0.68 V, (c) 0.88 V and (d) 0.95 V. The observed potential plateaus were considered to correspond to different coexisting Dy-Cu phases, respectively. Based on the result of open-circuit potentiometry, an alloy sample was prepared by potentiostatic electrolysis at 0.55 V for 4 h. From the XRD pattern of the sample, the alloy phase was identified as DyCu<sub>2</sub>. The other samples were prepared by potentiostatic electrolysis at 0.78 V and 1.50 V for 2 h with the formed DyCu<sub>2</sub> electrodes. In the sample obtained at 0.78 V, the existence of DyCu<sub>5</sub> was seen. The phase of the sample obtained at 1.50 V was transformed to Cu.

In order to consider the electrolysis potential for the separation of Dy, cyclic voltammetry was also conducted for a Cu wire electrode in a molten LiCl-KCl-DyCl<sub>3</sub>(0.50 mol%) system at 723 K. Figure 1 compares cyclic voltammograms recorded in the NdCl<sub>3</sub> added system and the DyCl<sub>3</sub> added system, which are represented with broken and solid curves, respectively. In the negative scan for the DyCl<sub>3</sub> added system, a cathodic current was observed from 0.65 V as a result of the formation of Dy-Cu alloys. In contrast, a cathodic current as a result of the

formation of Nd-Cu alloys was also observed from 0.65 V and was smaller than that as a result of the formation of Dy-Cu alloys. These results suggest that the separation of Dy can be achieved under 0.65 V.

Based on the results of cyclic voltammograms, alloy samples were prepared by potentiostatic electrolysis at 0.45-0.75 V for 1 h using Cu plate cathodes in a molten LiCl-KCl-NdCl<sub>3</sub>(0.50 mol%)-DyCl<sub>3</sub>(0.50 mol%) at 723 K. Figure 2 shows the mass ratio of Dy/Nd in the alloy samples measured by ICP-AES. The mass ratio of Dy/Nd in the alloy sample is 6-12 at 0.45-0.75 V. This result indicates the possibility of separating Dy in the molten LiCl-KCl-DyCl<sub>3</sub>-NdCl<sub>3</sub> system.

### References

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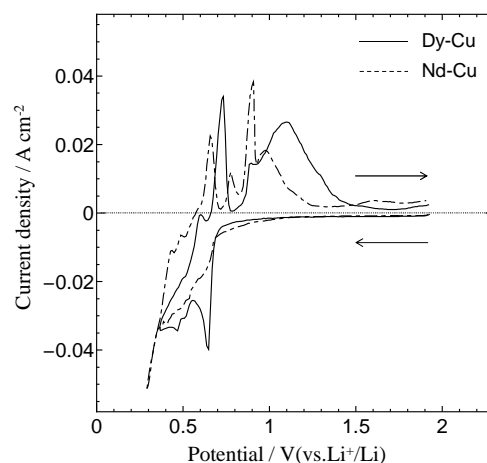


Fig. 1. Cyclic voltammograms for the Cu electrodes in a molten LiCl-KCl-DyCl<sub>3</sub> or NdCl<sub>3</sub> system (0.50 mol%) at 723 K. Scanning rate: 0.10 V s<sup>-1</sup>.

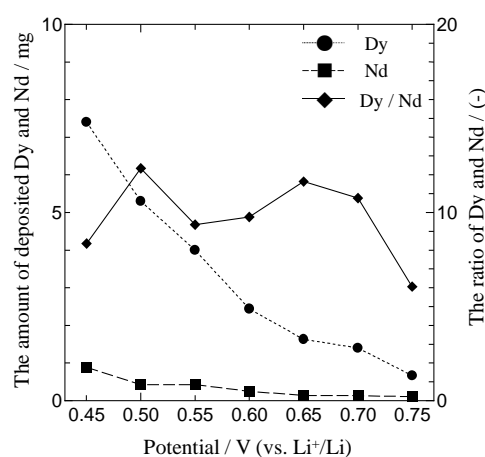


Fig. 2. Potential dependence of the amount of deposited Dy and Nd, and the mass ratio of Dy/Nd in alloy samples prepared in a molten LiCl-KCl-DyCl<sub>3</sub>-NdCl<sub>3</sub> system at 723 K.