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 scrap 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-DyCl3 system at 723 K. Figure 1 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-DyCl3-NdCl3 system.

Experimental

All experiments were performed in LiCl-KCl eutectic melts under dry argon atmosphere at 723 K. NdCl3 or DyCl3 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/AgCl electrode. All the potentials given hereafter were referred to Li+/ 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 0.64 V (vs. Li+/ Li) for 120 s in a molten LiCl-KCl-DyCl3 (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 0.78 V and 1.50 V for 2 h. The XRD pattern of the sample, the alloy phase was identified as DyCu4. The other samples were prepared by potentiostatic electrolysis at 0.78 V and 1.50 V for 2 h with the formed DyCu4. The samples were prepared at 0.78 V, the existence of DyCu4 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-DyCl3 (0.50 mol%) system at 723 K. Figure 1 compares cyclic voltammograms recorded in the NdCl3 added system and the DyCl3 added system, which are represented with broken and solid curves, respectively. In the negative scan for the DyCl3 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-NdCl3 (0.50 mol%)-DyCl3 (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-DyCl3-NdCl3 system.

References