

## ELECTROCHEMICAL SEPARATION OF Dy AND Nd FROM Nd MAGNET SCRAP IN A MOLTEN LiCl-KCl

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### Abstract

The Dy-Nd-Pr-Ni alloy sample was prepared by cathodic potentiostatic electrolysis at 0.65 V (vs. Li<sup>+</sup>/Li) for 1 h using a Ni plate in a molten LiCl-KCl-DyCl<sub>3</sub>-NdCl<sub>3</sub>-PrCl<sub>3</sub> system at 723 K. The highest mass ratio (Dy/Nd+Pr) in the alloy sample was observed to be 50 at 0.65 V. Anodic potentiostatic electrolysis at 2.20 V for 12 h was conducted using the Nd-Fe-B magnet electrode in a molten LiCl-KCl system. All elements were almost dissolved from the magnet, and the original form of the magnet disintegrated. After anodic potentiostatic electrolysis at 2.20 V, cathodic potentiostatic electrolysis was conducted at 1.00 V for 5 h using a Mo plate in order to remove the dissolved Fe from the bath. Finally, cathodic potentiostatic electrolysis was conducted at 0.65 V for 12 h using a Ni plate. The mass ratio of Dy/Nd in the alloy sample was determined to be about 18.

### Introduction

The use of rare earth (RE)-iron group (IG) alloys has increased significantly in a number of industrial fields over the past few decades. In particular, the demand for Dy-added Nd-Fe-B magnets is rapidly increasing because these magnets are indispensable for high-performance motors in electric vehicles (EVs) and hybrid electric vehicles (HEVs). These magnets need to possess sufficient thermal stability for use in such motors in high-temperature environments. The addition of Dy is necessary to improve the thermal stability of Nd-Fe-B magnets. However, there is the concern about a shortage of RE metals in general, and Dy, in particular, of the RE resources. Thus a worldwide need is being increasingly felt to augment the primary production of Nd and Dy by combining a suitable recycling method in order to reclaim these metals from their recyclable resources. In this context, it is worthwhile to mention that large Nd-Fe-B magnets are the only secondary resource materials as far as Dy is concerned. That is why, it is necessary to develop an inexpensive and environmentally friendly recovery/separation process for the recovery of Nd and Dy from a variety of scrap/waste magnets.

We are proposing a new separation and recovery process for the recovery of Nd and Dy from the RE scraps using molten salt and an alloy diaphragm concept in a molten salt system (Figure 1) [1-3]. This process is based on our previously discovered phenomena, i.e., “electrochemical implantation” and “electrochemical displantation” [4-6]. RE containing scrap is used as the anode. A RE-transition metal (TM) alloy is used as the diaphragm, which functions as a bipolar electrode. During electrolysis, all the RE metals in the anode are dissolved in the molten salt as RE ions. One or several specific RE ions are selectively reduced to form RE-TM alloys on the alloy diaphragm

according to their formation potentials and/or alloying rates. Subsequently, the RE atoms chemically diffuse through the alloy diaphragm and are re-dissolved into the molten salt as RE ions in the cathode compartment. The re-dissolved RE ions are finally deposited on either Mo or Fe cathode as RE metals. The RE ions remaining in the anode compartment can be electrodeposited by employing a second cathode leaving behind the impurities as anode mud/residue.

This new process was first applied to chloride melts, and the separation of Dy from Nd was investigated using Ni and Cu cathodes in molten LiCl-KCl-DyCl<sub>3</sub>-NdCl<sub>3</sub> systems [7-9]. The highest mass ratio of Dy/Nd in Dy-Nd-Ni alloy sample was found to be 72 by ICP-AES. The present study was the electrochemical formation of RE-Ni (RE=Dy, Nd, Pr) alloys using Ni electrodes in a molten LiCl-KCl-RECl<sub>3</sub> (0.50 mol% added) at 723 K. Furthermore, the anodic dissolution of RE (Dy, Nd, etc) using Nd-Fe-B magnet electrodes and electrowinning of Dy using Ni electrodes were carried out in a molten LiCl-KCl system at 723 K.

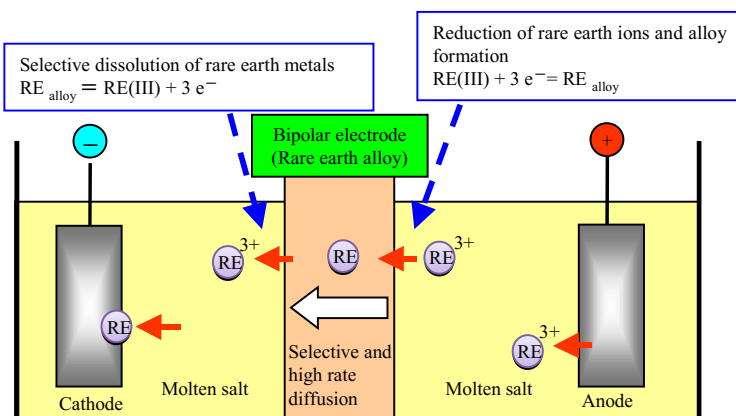


Figure 1. Schematic drawing of the process for separation and recovery of rare earth metals.

## Experimental

Anhydrous Reagent (AR) grade eutectic LiCl-KCl salt (58.5 mol% LiCl-41.5 mol% KCl) was placed in a recrystallized alumina crucible, which, in turn, was vacuum-treated for more than 24h at 473K, in order to remove moisture, prior to melting. Both the mixing of the electrolyte constituents and electrochemical measurements were carried out under dry argon atmosphere. 0.5 mol% DyCl<sub>3</sub>, NdCl<sub>3</sub> and PrCl<sub>3</sub> (99.9% pure, Kojundo Chemical Laboratory Co. Ltd.) was added to the eutectic salt to prepare the electrolyte. A chromel-alumel thermocouple was used to measure the temperature. A three electrode set up consisting of Nd-Fe-B plate (dimensions: 20mm long, 10 mm wide and 1.5mm thick, composition, mass%: 5Dy+20Nd+5.9Pr+65Fe+1B)/Ni wire (99% pure, 5mm long, 1mm dia.) WE, Mo/Ni plate type (99% pure, 20 mm long, 10 mm wide, 0.2 mm thick) CE and Ag-(1mol%) AgCl RE was used for the electrochemical measurements. The potential of the RE was calibrated against the in situ Li<sup>+</sup>/Li electrode, prepared by depositing Li metal on a Mo wire (during the electrochemical measurements). Potentiostatic electrolysis was performed at 723K to prepare the electrodeposited samples. The samples were characterized and evaluated by SEM-EDS, and ICP-AES instruments.

## Results and Discussion

### Electrochemical Formation of RE-Ni (RE-Dy, Nd and Pr) Alloys

Figure 2 compares the cyclic voltammograms of  $\text{DyCl}_3$ ,  $\text{NdCl}_3$  and  $\text{PrCl}_3$ . Appearance of a relatively larger cathodic current (the peak current being at  $\sim 0.40$  V) at 0.70 V (with a corresponding anodic peak during the reverse scan) indicated the selective removal of Dy (from Nd and Pr). In contrast, both Nd and Pr exhibited cathode current responses at 0.60 V. Besides, the appearance of smaller cathodic current peaks at  $\sim 0.65$  V were probably due to the occurrence of  $\text{Nd(III)/Nd(II)}$  and  $\text{Pr(III)/Pr(II)}$  reactions. The CV suggests that the application of a voltage in the range 0.60-0.70 V can potentially remove Dy from the mixture of Nd and Pr.

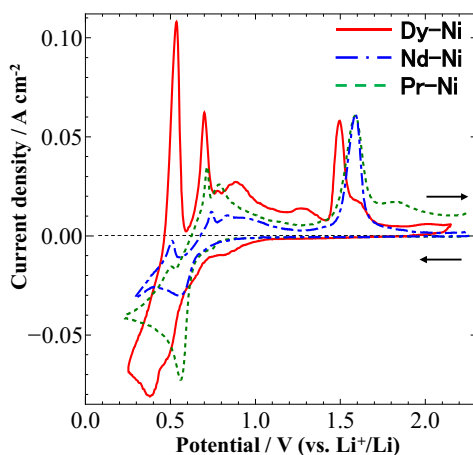


Figure 2. Cyclic voltammograms with Ni electrodes in a molten  $\text{LiCl-KCl-DyCl}_3/\text{NdCl}_3/\text{PrCl}_3$  (0.50 mol% added) at 723 K. Scan rate:  $0.05 \text{ V s}^{-1}$ . Surface area:  $0.16 \text{ cm}^2$ .

Based on the CV response (Figure 2), we have already reported the possibility of separation of Dy from Nd, using a Ni electrode, from the  $\text{LiCl-KCl-DyCl}_3\text{-NdCl}_3$  electrolyte system [8]. In the present studies, the specific focus was on the possibility of removal of Dy from Pr and Nd from Pr. Further experiments were carried out, at 0.55-0.70 V for 1 h using Ni plate-type cathode, to examine the extent of removal of Dy from the mixture of Dy, Nd and Pr. Figure 3 shows the Dy/Pr mass ratio in the electrodeposited alloy samples, measured by ICP-AES. The highest value for the ratio was observed to be formed at an operating voltage of 0.70 V. When the studies were extended to examine the separation efficiency between Nd and Pr, it was observed that no separation could be possible as the mass ratio stayed unity at all operating voltages (Figure 4). Experiments aimed at separating Dy from a mixture of Nd and Pr revealed that a highest separation quotient (Dy/Nd+Pr) of 50 could be achieved at an operating voltage of 0.65V (Figure 5).

These results indicated the possibility of separating Dy from Nd and Pr by controlling electrolysis potential in a molten  $\text{LiCl-KCl-DyCl}_3\text{-NdCl}_3\text{-PrCl}_3$  system.

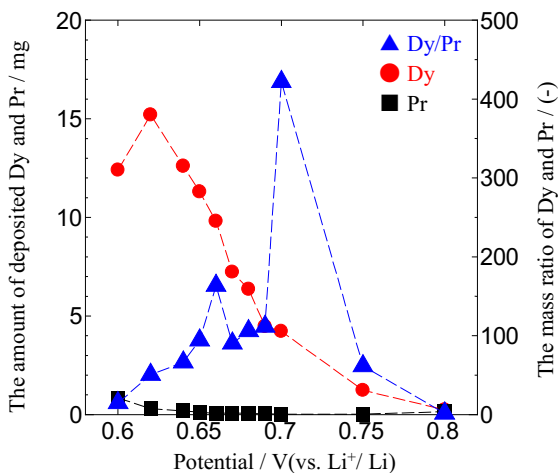


Figure 3. Potential dependences of the amounts of deposited Dy and Pr, and of the mass ratio of Dy/Pr, in a molten LiCl-KCl-DyCl<sub>3</sub>(0.50 mol% add)-PrCl<sub>3</sub>(0.50 mol% added) at 723 K.

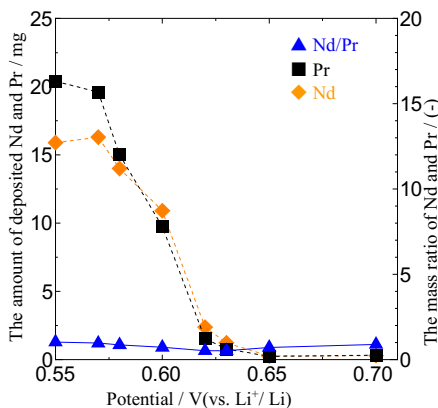


Figure 4. Potential dependences of the amounts of deposited Nd and Pr, and of the mass ratio of Nd/Pr, in a molten LiCl-KCl-NdCl<sub>3</sub>(0.50 mol% add)-PrCl<sub>3</sub>(0.50 mol% added) at 723 K.

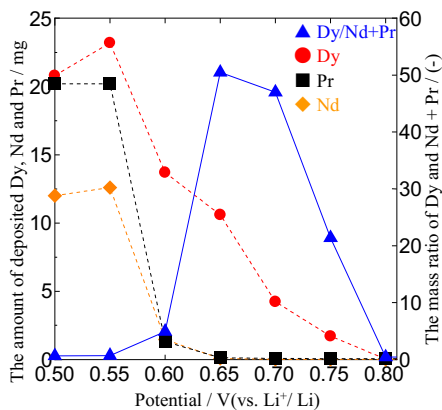


Figure 5. Potential dependences of the amounts of deposited Dy, Nd and Pr, and of the mass ratio of Dy/Nd+Pr, in a molten LiCl-KCl-DyCl<sub>3</sub>(0.50 mol% add)-NdCl<sub>3</sub>(0.50 mol% add)-PrCl<sub>3</sub>(0.50 mol% added) at 723 K.

#### Recovery of Dy under Potentiostatic Electrolysis Condition

A combination of anodic dissolution (at 2.20 V for 12 h) and cathodic deposition (at 1.00 V for 5 h) was carried out to deposit the dissolved Fe (from the electrolyte) onto a Mo plate prior to

the separation of Dy from the RE mixtures. Fe, from the Nd-Fe-B magnet, quickly dissolved in the electrolyte upon anodic polarization. The Fe removal was followed up by another potentiostatic experiment, at 0.65 V for 4 and 12 h (Figures 6 and 7 respectively), to remove Dy from the electrolyte and form of Dy-Ni alloy in situ at the Ni plate. The EDS measurements showed the Dy/Nd ratio to be 11 (after 4 h of electrolysis, Figure 6) and 18 (after 12h of electrolysis, Figure 7). As predicted, Pr was observed to be present in both the (Dy-Nd) alloy deposits. These results further confirmed that the separation of Dy, from a mixture of Dy, Nd and Pr, can be achieved under a set of optimum operating conditions.

In order to recover residual Nd and Pr from the electrolyte (after the removal of Dy), further electrolysis was carried out at 0.65 V for 4 h and 12 h respectively. Figure 8 shows the cross-sectional SEM image of the sample obtained at 0.60 V and 1.5 h. The mass ratio of Dy:Nd:Pr in the alloy was determined to be 11:8.4:1. This analysis clearly indicated that quantitative recovery of Dy could not be achieved even after carrying out electrolysis at 0.65 V for the duration of 16 h. A mass ratio of Dy:Nd:Pr as 1.9:4.7:1.0 indicated that it was possible to deposit Nd and Pr onto nickel cathode at an operating voltage of 0.55 V and an electrolysis duration of 3 h (Figure 9).

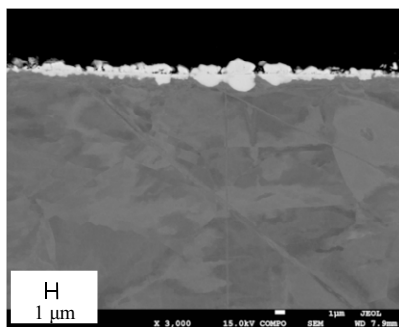


Figure 6. Cross-sectional SEM image of the sample prepared by cathodic potentiostatic electrolysis using a Ni electrode at 0.65 V for 4 h in a molten LiCl-KCl system at 723 K.

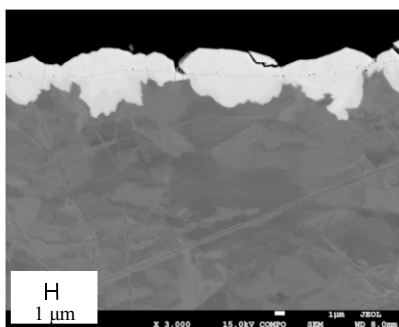


Figure 7. Cross-sectional SEM image of the sample prepared by cathodic potentiostatic electrolysis using a Ni electrode at 0.65 V for 12 h in a molten LiCl-KCl system at 723 K.

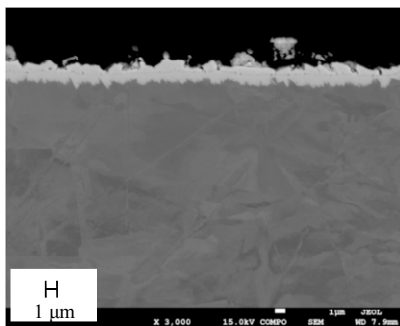


Figure 8. Cross-sectional SEM image of the sample prepared by cathodic potentiostatic electrolysis using a Ni electrode at 0.60 V for 1.5 h in a molten LiCl-KCl system at 723 K.

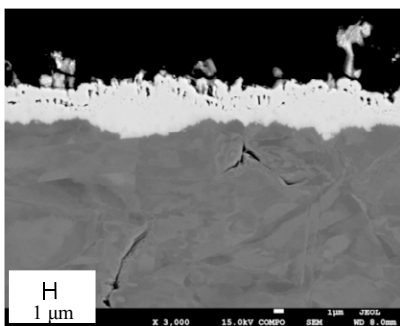


Figure 9. Cross-sectional SEM image of the sample prepared by cathodic potentiostatic electrolysis using a Ni electrode at 0.55 V for 3 h in a molten LiCl-KCl system at 723 K.

#### Anodic Dissolution Behavior of the Nd-Fe-B Magnet

The Nd-Fe-B magnet was wrapped in a nickel wire and then subjected to anodic dissolution at 1.70-2.20 V for 12 h. Figure 10 shows the cross-sectional SEM image of the sample retrieved after dissolution at 1.70 V. The EDS analysis showed a variation in the dissolution pattern. It was observed that the Nd, present in the outer layer underwent preferential dissolution leaving the Nd present in the inner layer untouched. This might have happened because of the large cracks, found between inner and outer layer, generated during the electrochemical dissolution process. When the anodic dissolution was carried out at a comparatively higher voltage (2.20 V), all the three elements underwent complete dissolution and there was hardly any magnet sample left in the nickel wire.

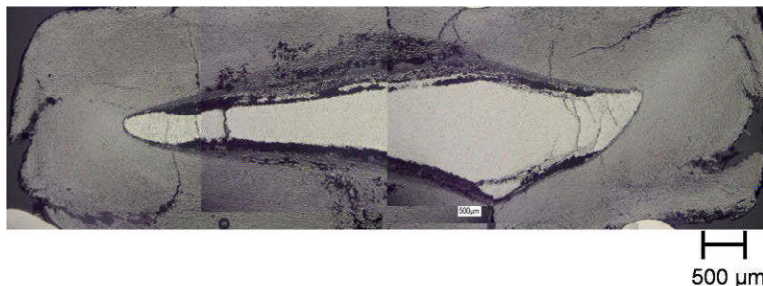


Figure 10. Cross-sectional SEM image of the sample prepared by anodic potentiostatic electrolysis using a Nd-Fe-B magnet electrode at 1.70 V for 12 h in a molten LiCl-KCl system at 723 K.

### Conclusions

The electrochemical formation of RE-Ni (RE=Dy, Nd, Pr) alloys using Ni electrodes was investigated in a molten LiCl-KCl-RECl<sub>3</sub> (0.50 mol%) at 723 K. Furthermore, the anodic dissolution of RE (Dy, Nd, etc) using Nd-Fe-B magnet electrodes and electrowinning of Dy using Ni electrodes were carried out in a molten LiCl-KCl system at 723 K. The results could be summarized as follows:

1. The alloy sample was prepared by potentiostatic electrolysis at 0.65 V for 1 h using a Ni cathode in a molten LiCl-KCl-DyCl<sub>3</sub>-NdCl<sub>3</sub>-PrCl<sub>3</sub> system. The highest mass ratio of Dy/Nd+Pr in the alloy sample measured by ICP-AES was determined to be 50 at 0.65 V.
2. Anodic potentiostatic electrolysis at 1.70 V and 2.20 V for 12 h were conducted using Nd-Fe-B magnet electrodes wrapped Ni wires. It was found that RE in the outer layer was selectively dissolved but RE in the inner layer remained undissolved from the EDX analysis of the cross-section of the sample obtained at 1.70 V. The sample obtained at 2.20 V was almost dissolved, and the original form of the magnet disintegrated.
3. After anodic potentiostatic electrolysis at 2.20 V for 12 h using the Nd-Fe-B magnet and cathodic potentiostatic electrolysis at 1.00 V for 5 h using a Mo plate, cathodic potentiostatic electrolysis was conducted at 0.65 V for 12 h using a Ni plate. From the EDX analysis of formed alloy, the mass ratio of Dy/Nd in the alloy sample was about 18.

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