



Electrochemical Formation of Nd–Ni Alloys in Molten $\text{CaCl}_2\text{–NdCl}_3$

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The electrochemical formation of Neodymium–Nickel (Nd–Ni) alloys was investigated in a molten $\text{CaCl}_2\text{–NdCl}_3$ (1.0 mol%) system at 1123 K. Cyclic voltammograms for Molybdenum (Mo) and Ni electrodes showed the electrodeposition/dissolution of metallic Nd and the formation/dissolution of Nd–Ni alloys, respectively. The equilibrium potential of Nd^{3+}/Nd was determined at 0.27 V (vs. Ca^{2+}/Ca) by open-circuit potentiometry for a Mo electrode. The potentials of 0.48, 0.68, and 0.95 V, corresponding to the two-phase coexisting states of ($\text{NdNi}_2 + \text{NdNi}_3$), ($\text{NdNi}_3 + \text{NdNi}_5$), and ($\text{NdNi}_5 + \text{Ni}$), respectively, were confirmed using energy-dispersive X-ray spectroscopy and X-ray diffraction of the Ni electrode electrolyzed samples. The optimum electrolysis conditions for the Nd and Dysprosium (Dy) separation were discussed, and the standard Gibbs energies of formation were calculated for Nd–Ni alloys.

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Throughout the world, rare earth elements (REEs) are an essential ingredient for industrial materials. Unique properties such as hydrogen storage, permeability, catalytic properties, and magnetism are endowed from REEs. Among these remarkable physical and chemical properties, the magnetism of Neodymium (Nd) magnets, which are the strongest permanent magnets, has recently been under focus due to the popularization of battery electric vehicles (BEVs) and hybrid electric vehicles (HEVs). The addition of Dysprosium (Dy) is necessary to improve the thermal stability of the Nd magnet for high-performance motors in BEVs and HEVs.¹ The increased focus on environmental-friendly technology has led to high demands for BEVs and HEVs. Hence, the demand for Nd and Dy is also expected to increase.

Contrary to the increased demand for Nd magnets, the industrial supply for REEs is unstable. Sharp price fluctuations and uneven distributions pose obstacles to stabilize long-term supply and demand. In 2019, China, Brazil, Vietnam, and Russia dominated with more than 80% of globally proven REE reserves.² The combination of hydrometallurgy leaching and solvent extraction is the only practical recycling process currently used. Although the method is used for on-site process waste recycling in Nd–Fe–B magnet manufacturing plants,³ multistep processes, high energy consumption, and high environmental load are the disadvantages because it is basically the method for ore processing. Additionally, while waste emission from electronic products (e-waste), which includes high concentrations of REEs, has increased rapidly, its recycling is yet to be industrialized. Due to this, the industry requires a new REE recycling process to be developed from secondary resources.

Several researchers have proposed various REE recycling methods^{4–21} but the separation between REEs was not the focus of their research. We have proposed a new separation and recovery process using the selective formation of rare earth and transition metal (TM) alloys in molten salts.^{22,23} Before RE–TM alloy fabrication, REEs are extracted from the scrap of Nd magnets by immersing it in a low-vapor-pressure molten salt under vacuum. This allows the Nd concentration to decrease during evaporation.²²

When the Nd concentration reduces to that of Dy, the mixed molten salt is used to fabricate RE–TM alloys.²³ As the formation potentials of RE–TM alloys and the diffusion rate of RE in the RE–TM alloys are different for Nd and Dy, a high separation ratio between Nd and Dy is obtained. Based on this process, we have investigated the formation of RE–Ni (RE = Nd, Dy) alloys and the separation of Nd and Dy in molten LiCl–KCl at approximately 700 K,^{24–26} NaCl–KCl at 973 K,^{27–29} and LiF–CaF_2 at 1123 K.^{30–32} We found the desirable separation ratio in the chloride system; for example, the maximum separation ratio Dy/Nd was 72 and 25 in LiCl–KCl ²⁶ and NaCl–KCl ,²⁹ respectively. Although a considerably high formation rate of RE–TM alloys was achieved at over $200 \mu\text{m h}^{-1}$ in the LiF–CaF_2 system, the Dy/Nd separation ratio was limited to 6.³² To summarize the previous studies, we achieved high separation ratios in chloride melts and high alloy formation rates at high operating temperatures. Thus, finding a chloride melt, which operates at high temperatures, is a rational approach to achieve a high separation ratio and alloy formation rate. We chose CaCl_2 ($T_m = 1055 \text{ K}$) as the electrolyte due to its lower vapor pressure as compared to those of the alkali and alkaline earth metal chlorides. As previously reported the electrochemical formation of Dy–Ni alloys in a molten $\text{CaCl}_2\text{–DyCl}_3$ (1.0 mol%) system at 1123 K,³³ we used the same approach for Nd–Ni alloys in a molten $\text{CaCl}_2\text{–NdCl}_3$ (1.0 mol%) system at 1123 K for the present study.

First, the electrochemical behavior of Nd^{3+} ions at the Mo and Ni electrodes was investigated by cyclic voltammetry (CV). Then, the two-phase coexisting potentials of Nd–Ni alloys were estimated by open-circuit potentiometry (OCP). Based on these results, Nd–Ni alloy samples were prepared at various potentials. X-ray diffraction (XRD) was used to identify the formed Nd–Ni alloy phase. Cross-sections of the samples were observed by scanning electron microscopy (SEM) and analyzed by energy-dispersive X-ray spectroscopy (EDX). The appropriate separation conditions are discussed by comparing the two-phase coexisting potentials for Nd–Ni and Dy–Ni alloys. Finally, the standard Gibbs energies of formation for each Nd–Ni alloy were calculated from the two-phase coexisting potentials and compared with the reported CALPHAD values.³⁴

Experimental

The electrolysis setup and produce were obtained from a previous report.³³ Powdery CaCl_2 (Kojundo Chemical Laboratory Co., Ltd., 99.9%) was loaded in a graphite crucible (Sanko Co., Ltd., IG-110,

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i.d.: 90 mm, height: 120 mm) and dehydrated in a vacuum oven at 453 K for 72 h. Then, the crucible was placed at the bottom of a stainless-steel vessel in an airproof Kanthal container for further dehydration in an Ar atmosphere glove box under vacuum at 773 K for 24 h. The experiment was carried out at 1123 K in a dry argon atmosphere with a flow rate of 100 ml min⁻¹. After the blank system was measured, powdery and anhydrous NdCl₃ (Kojundo Chemical Laboratory Co., Ltd., 99.9%) was directly added to the melt to form an Nd³⁺ ion source with 1.0 mol% concentration.

Two types of working electrodes were used: flag electrodes (diameter: 3.0 mm, thickness: 0.1 mm, lead wire diameter: 0.2 mm) for CV and OCP measurements, and plate electrodes (5 mm width × 20 mm length × 0.1 mm thickness) for sample preparation. Mo (Nilaco Corp., >99%) and Ni (Nilaco Corp., >99%) were used as working electrode materials. The counter electrode was a carbon rod (Sanko Co. Ltd., diameter 7 mm × length 520 mm). A Ni wire (Nilaco Corp., >99%, diameter: 1.0 mm), immersed in molten CaCl₂ containing 1.0 mol% NiCl₂ (Alfa Aesar Corp., 98%), was set in a mullite tube (Nikkato Corp., o.d. × i.d. × length = 6 mm × 4 mm × 500 mm, 56% Al₂O₃–40% SiO₂; HB grade) and used as the Ni²⁺/Ni reference electrode. The reference electrode potential was occasionally calibrated as per the Ca²⁺/Ca dynamic reference electrode potential, which was prepared by the Calcium (Ca) metal electrodeposition on a Mo electrode. All the potentials in this study were obtained as per this Ca²⁺/Ca electrode potential. An electrochemical measurement system (Hokuto Denko Corp., HZ-7000) connected to a computer was used for all measurements.

The alloy samples, prepared by electrolysis of Ni plates, were washed with deionized water to remove solidified chloride salts from the surface, and then rinsed with ethanol (FUJIFILM Wako Pure Chemical Corp., 99.5%). The samples were analyzed by XRD (Rigaku Corp., Ultima IV) using Cu-Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. For cross-sectional SEM observation (Thermo Fisher Scientific Inc., Phenom Pro Generation 5) and EDX analysis (Thermo Fisher Scientific Inc., SEI200–8001), samples were embedded in acrylic resin and polished with emery papers (#320 and #600), polycrystalline diamond suspensions (3 μm and 9 μm), and buffing compound (Micro Polish II, 0.3 μm, Buehler).

Results and Discussion

Cyclic voltammetry.—A Mo electrode was used to measure the potentials of Ca²⁺/Ca and Nd³⁺/Nd as alloys are non-existent in binary Mo–Ca and Mo–Nd systems at 1123 K.³⁵ Figure 1 shows the cyclic voltammogram comparison for a Mo electrode in molten CaCl₂ before (black line) and after (red line) the addition of 1.0 mol% NdCl₃. For blank measurement, only a pair of rapid cathodic and anodic current is observed, which should correspond to Ca deposition/dissolution. After NdCl₃ addition and besides the currents assigned to Ca deposition/dissolution, a new anodic current increases at approximately 0.3 V (vs. Ca²⁺/Ca). Based on Mo properties, the current should be interpreted as the dissolution of Nd metal. The cathodic current of the Nd deposition may be overcome by the rapid increase in the cathodic current due to the formation of Ca metal fog from approximately 0.2 V.³³

Figure 2 presents the cyclic voltammograms measured for a Ni electrode under the same conditions. For blank measurements, the Ca metal fog formation current³³ is observed. After NdCl₃ addition, the cathodic current increase from approximately 1.0 V suggesting the formation of Nd–Ni alloys. The Nd–Ni system phase diagram³⁶ (Fig. 3) shows four intermetallic compounds (NdNi₂, NdNi₃, Nd₂Ni₇, and NdNi₅) and a liquid alloy at 1123 K. The four Nd–Ni alloys are expected to form electrochemically. Several anodic peaks/shoulders are observed under an anodic sweep, which could be caused by Nd dissolution from the different Nd–Ni alloys.

Open-circuit potentiometry.—In our previous study,^{25,27,30,33} OCP was selected as the appropriate method to determine the

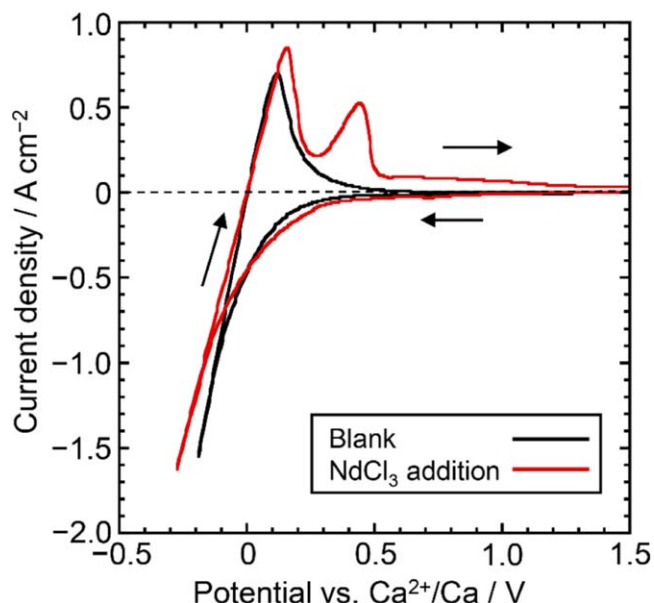


Figure 1. Cyclic voltammograms for a Mo flag electrode in molten CaCl₂ before and after the addition of 1.0 mol% NdCl₃ at 1123 K. Scan rate: 100 mV s⁻¹.

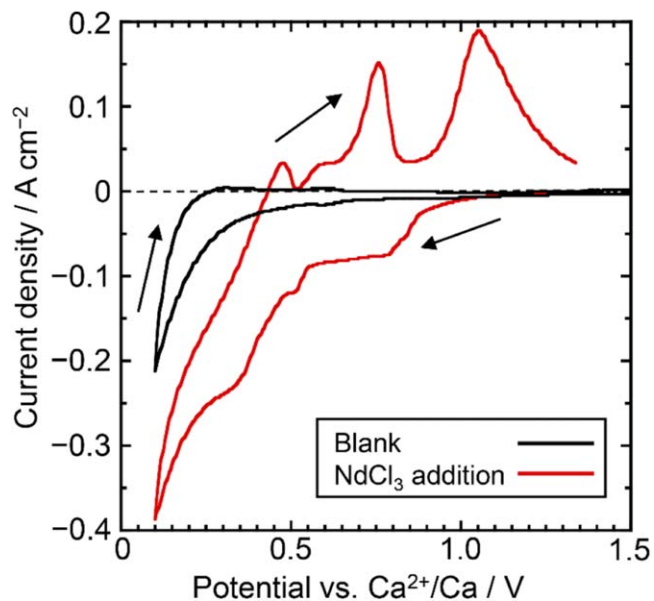


Figure 2. Cyclic voltammograms for a Ni flag electrode in molten CaCl₂ before and after the addition of 1.0 mol% NdCl₃ at 1123 K. Scan rate: 100 mV s⁻¹.

equilibrium potential of RE³⁺/RE and the two-phase coexisting potentials of RE–Ni alloys. To determine the Nd³⁺/Nd potential, the measurement was conducted, using a Mo electrode in molten CaCl₂, before and after the addition of NdCl₃. As shown in Fig. 4, after galvanostatic electrolysis at –1.0 A cm⁻² for 30 s, an additional potential plateau appears at 0.27 V after the NdCl₃ addition. This corresponds to the equilibrium potential of Nd³⁺/Nd.

In our previous study, Ca–Ni alloys were formed at 0.13 V in this system.³³ To avoid the influence of Ca–Ni alloys and Nd metal, OCP measurement for a Ni electrode was conducted after the formation of Nd–Ni alloys at 0.30 V for 150 s. As shown in Fig. 5, three potential plateaus are observed at 0.48, 0.68, and 0.95 V, which were determined from the smallest differential coefficient points. These

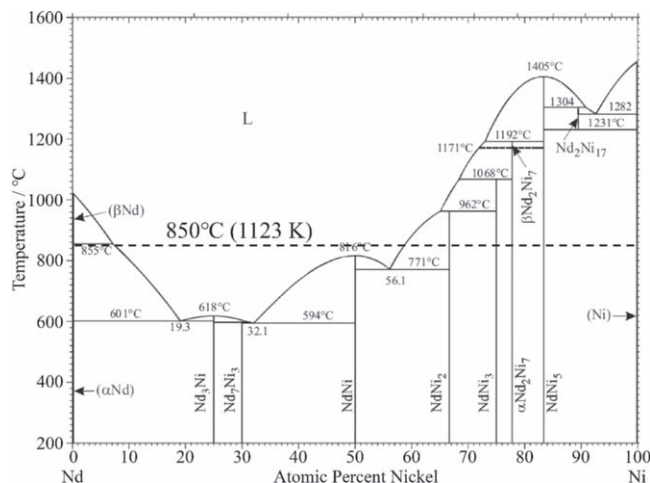


Figure 3. Binary phase diagram for the Nd–Ni system.³⁶

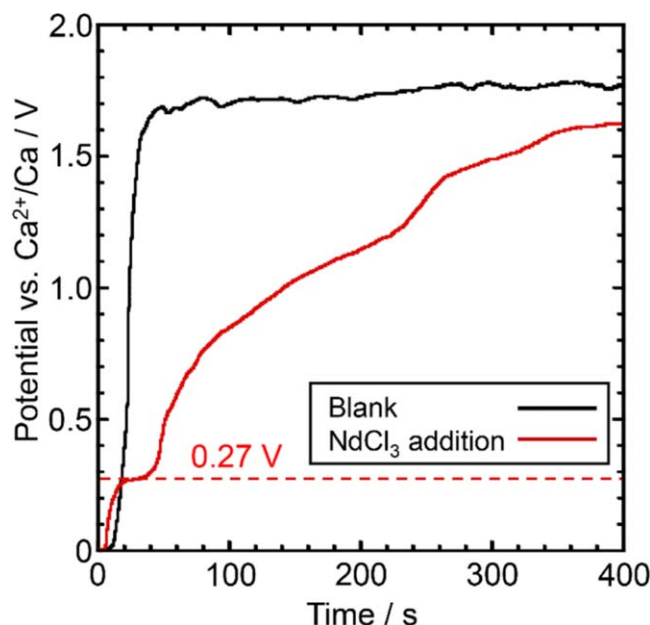


Figure 4. Open-circuit potentiograms for a Mo flag electrode after galvanostatic electrolysis at -1.0 A cm^{-2} for 30 s in molten CaCl_2 before and after the addition of 1.0 mol% NdCl_3 at 1123 K.

plateaus correspond to the two-phase coexisting state potential of different Nd–Ni alloys.

Preparation and characterization of Nd–Ni alloys.—To obtain more information on Nd–Ni alloy formation, samples were prepared by potentiostatic electrolysis at 0.30, 0.50, 0.80, and 1.00 V.

Figures 6a and 6b show a cross-sectional SEM image with EDX analysis and an XRD pattern, respectively, for the sample prepared by the potentiostatic electrolysis at 0.30 V for 15 min. Three layers are observed through the cross-sectional SEM image. According to the EDX analysis, the atomic composition for Nd:Ni at point (1), (2), and (3) are Nd:Ni = 0:100, 26.50:73.50, and 33.87:66.13, respectively. The three layers would correspond to Ni, NdNi_3 , and NdNi_2 . The different alloy layers were formed due to the varying Nd diffusion rates. The XRD pattern confirmed that the sample has a NdNi_2 surface layer. As NdNi_2 is formed from the highest Nd concentrated Nd–Ni alloy, it is the thermodynamically stable phase at 0.30 V.

Figure 7 shows the analysis of the sample electrolyzed at 0.50 V for 60 min Fig. 7a shows the cross-sectional SEM image and EDX analysis with two alloy layers on the Ni substrate. (2) The Nd:Ni

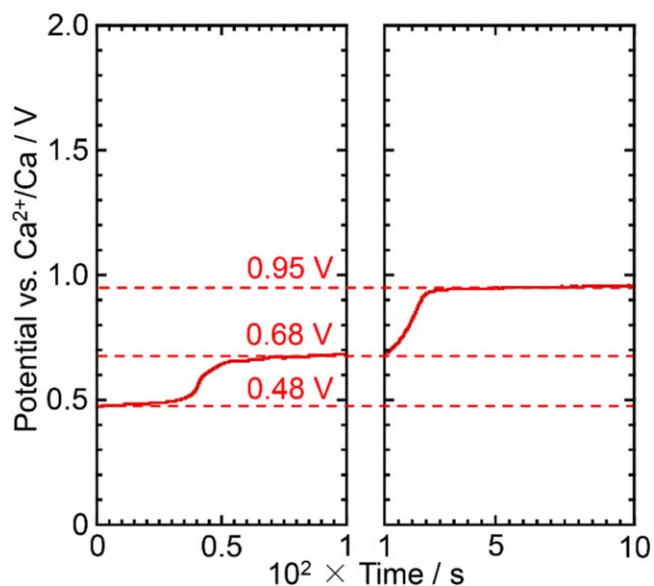


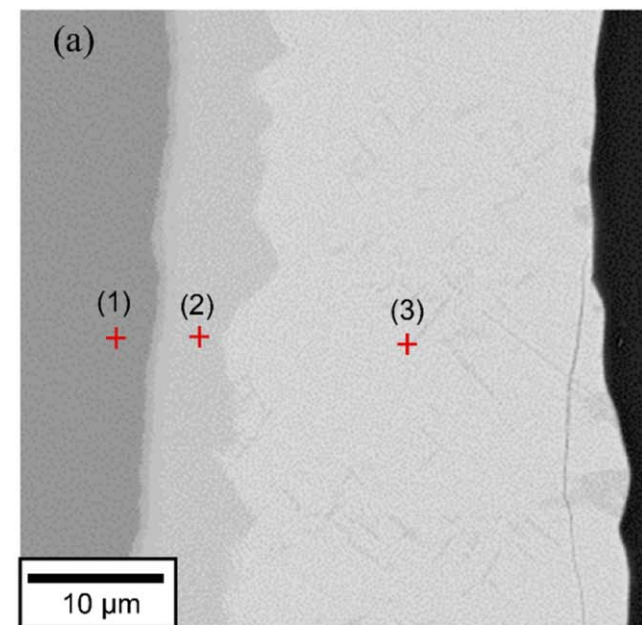
Figure 5. Open-circuit potentiogram at a Ni flag electrode after potentiostatic electrolysis at 0.30 V for 150 s in molten CaCl_2 – NdCl_3 (1.0 mol%) at 1123 K.

composition of the middle layer is 18.02:81.98, which is close to the NdNi_5 composition. (3) The outer alloy layer has an Nd:Ni composition of 25.85:74.15, which is similar to the NdNi_3 composition. Figure 7b shows the obtained XRD pattern, which confirms the NdNi_3 outer alloy layer. The XRD pattern for the NdNi_3 phase was calculated by the PowderCell program using the reported crystallographic parameters. Lattice parameters for NdNi_3 were reported by A.V. Virkar and A. Raman³⁷ and positional parameters of PuNi_3 atoms, which are isostructural with NdNi_3 were reported by D.T. Cromer and C.E. Olsen.³⁸ Finally, the thermodynamically stable phase at 0.50 V is confirmed as NdNi_3 . From the analysis results of samples prepared at 0.30 and 0.50 V, the potential plateau at 0.48 V in Fig. 5 corresponds to the two-phase coexisting state of NdNi_2 and NdNi_3 .

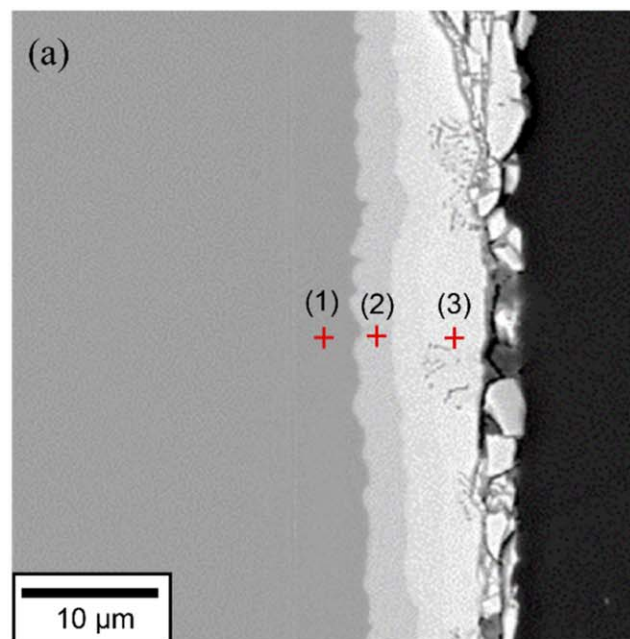
To confirm the coexisting phase at 0.68 V in Fig. 5, the sample was prepared at 0.80 V for 60 min Figs. 8a and 8b show the cross-sectional SEM image with EDX analysis and an XRD pattern for the sample, respectively. A thin alloy layer is observed in the SEM image. The EDX (Nd:Ni = 17.56:82.44 at point (2) and 17.92:82.08 at point (3)) and XRD analyses confirmed the NdNi_5 alloy layer. As the alloy layer thickness is below 5 μm , XRD peaks assigned to the Ni substrate are observed in the XRD pattern. Thus, NdNi_5 is the thermodynamically stable phase at 0.80 V, and the potential plateau at 0.68 V corresponds to the two-phase coexisting state of NdNi_3 and NdNi_5 .

Finally, to confirm that the two-phase coexisting state of Nd–Ni and Ni metal is shown by the plateau at 0.95 V in Fig. 5, the sample was prepared at 1.00 V for 60 min Figs. 9a and 9b show a cross-sectional SEM image with EDX analysis and an XRD pattern for the sample, respectively. These analyses did not show the formation of an alloy. Thus, Ni is the thermodynamically stable phase at 1.00 V and the potential plateau at 0.95 V in Fig. 5 corresponds to the two-phase coexisting state of NdNi_5 and Ni.

Upon comparison with previous studies, which confirmed the Nd–Ni alloy formation,^{27,30,39} the Nd_2Ni_7 formation was not confirmed. It might be caused by the slow formation rate of Nd_2Ni_7 and the high transition rate of NdNi_5 . The NdNi_2 formation rate is over $100 \mu\text{m h}^{-1}$, which is equivalent to that of the fluoride system at the same temperature.³⁰ Based on the aforementioned results, the three potential plateaus at 0.48, 0.68, and 0.95 V obtained during the OCP measurement correspond to the two-phase coexisting states of (NdNi_2 + NdNi_3), (NdNi_3 + NdNi_5), and (NdNi_5 + Ni), respectively.



EDX (1) Nd : Ni = 0 : 100
(2) Nd : Ni = 26.50 : 73.50
(3) Nd : Ni = 33.87 : 66.13
(at%)



EDX (1) Nd : Ni = 0 : 100
(2) Nd : Ni = 18.02 : 81.98
(3) Nd : Ni = 25.85 : 74.15
(at%)

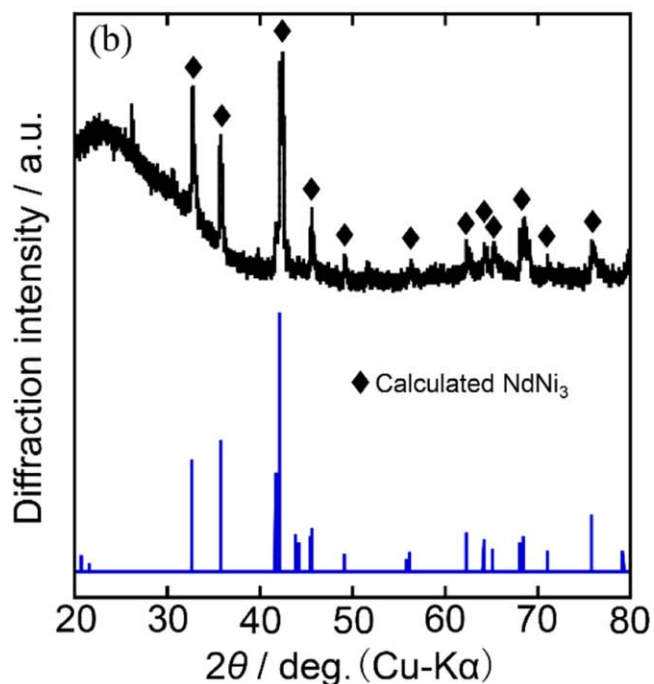
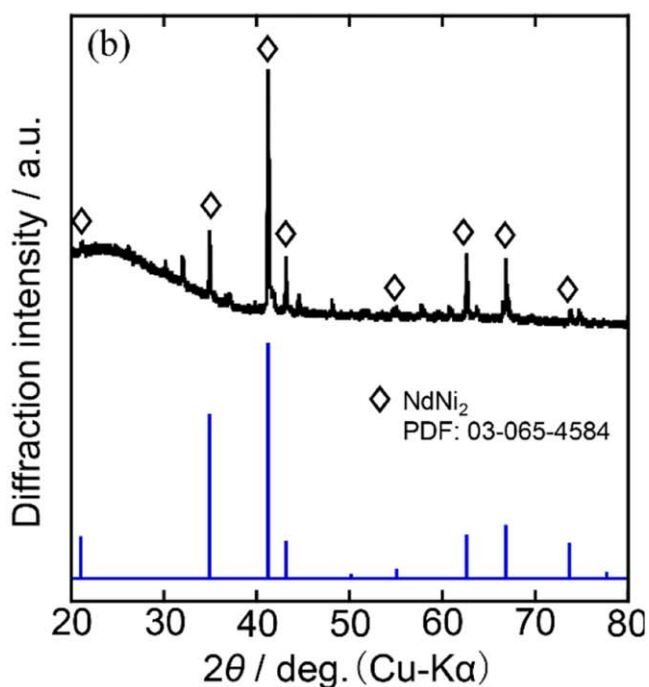
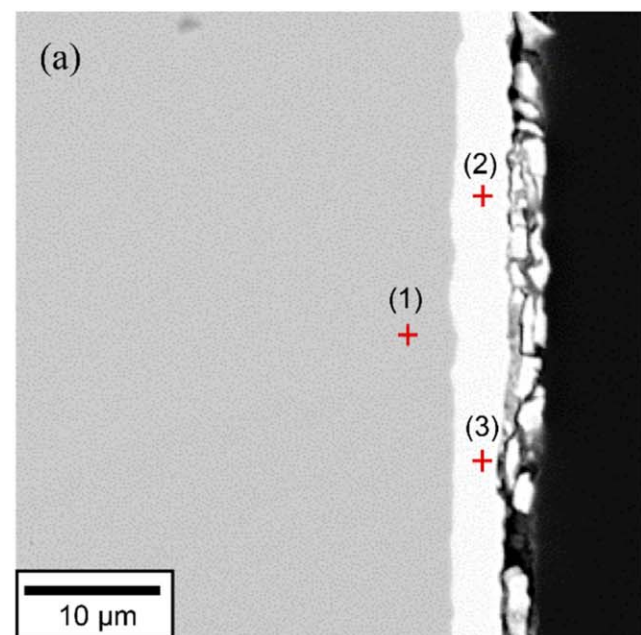


Figure 6. (a) A cross-sectional SEM image with EDX analysis and (b) an XRD pattern of the sample obtained by potentiostatic electrolysis with a Ni electrode at 0.30 V for 15 min in a molten $\text{CaCl}_2\text{--NdCl}_3$ (1.0 mol%) system at 1123 K.

Table I lists the equilibrium reactions of RE (RE = Nd, Dy) metal, RE–Ni alloys, and their corresponding potentials for each reaction in molten $\text{CaCl}_2\text{--RECl}_3$ (1.0 mol%) at 1123 K. As RENi_2 alloys have a considerably high formation rate, we compared the potential difference between RENi_2 alloys and RE metals. As the

Figure 7. (a) A cross-sectional SEM image with EDX analysis and (b) an XRD pattern of the sample obtained by potentiostatic electrolysis with a Ni electrode at 0.50 V for 60 min in a molten $\text{CaCl}_2\text{--NdCl}_3$ (1.0 mol%) system at 1123 K.

DyNi_2 formation potential is more positive than that of NdNi_2 by 0.14 V, and the deposition potential of Dy is more positive than that of Nd by 0.06 V, more efficient Dy/Nd separation is expected by DyNi_2 alloy manufacturing.



EDX (at%)
 (1) Nd : Ni = 0 : 100
 (2) Nd : Ni = 17.56 : 82.44
 (3) Nd : Ni = 17.92 : 82.08

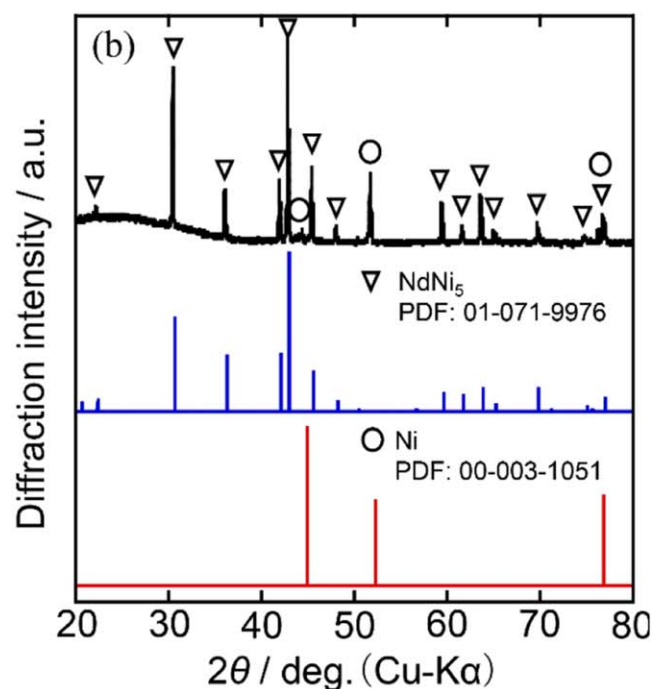
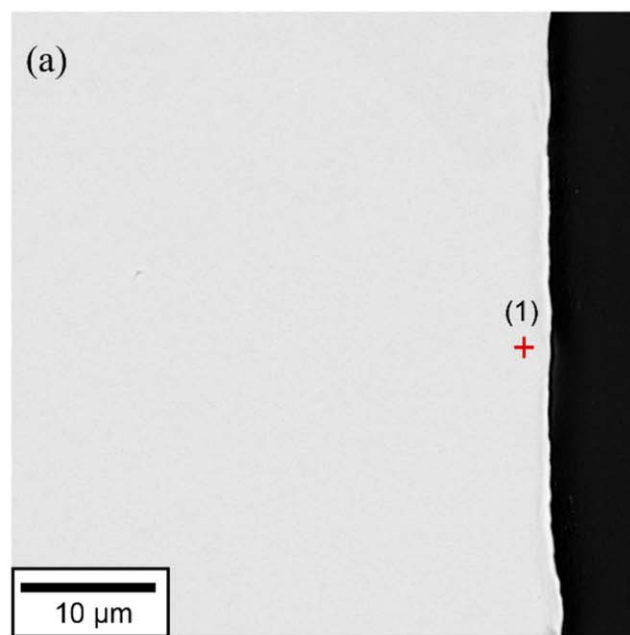


Figure 8. (a) A cross-sectional SEM image with EDX analysis and (b) an XRD pattern of the sample obtained by potentiostatic electrolysis with a Ni electrode at 0.80 V for 60 min in a molten $\text{CaCl}_2\text{--NdCl}_3$ (1.0 mol%) system at 1123 K.

Calculation of standard Gibbs energies of formation.—The standard Gibbs energies of formation for Nd–Ni alloys were calculated using the previously described method.²⁵ Since Nd_2Ni_7 was not confirmed, the obtained values were based on the metastable states of the system. First, the partial molar Gibbs energy of Nd



EDX (at%)
 (1) Nd : Ni = 0 : 100

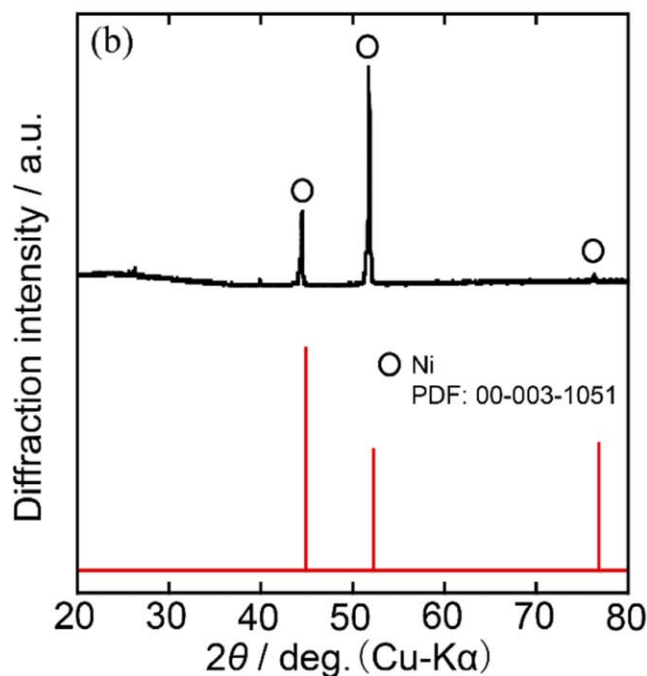


Figure 9. (a) A cross-sectional SEM image with EDX analysis and (b) an XRD pattern of the sample obtained by potentiostatic electrolysis with a Ni electrode at 1.00 V for 60 min in a molten $\text{CaCl}_2\text{--NdCl}_3$ (1.0 mol%) system at 1123 K.

($\Delta\bar{G}_{\text{Nd}}$) and activities of Nd (a_{Nd}) were calculated from the Nd–Ni alloy formation potentials (E vs. Nd^{3+}/Nd / V) listed in Table I. Then, the Ni activities (a_{Ni}), in the Nd–Ni alloys with reference to pure solid Ni as the standard state were calculated by the Gibbs–Duhem equation. The partial molar Gibbs energies of Ni ($\Delta\bar{G}_{\text{Ni}}$)

Table I. Equilibrium reactions and corresponding potentials for RE–Ni alloys and metallic RE in molten $\text{CaCl}_2\text{--RECl}_3$ (1.0 mol%) at 1123 K.

Equilibrium reactions	Potential vs. $\text{Ca}^{2+}/\text{Ca/V}$		Potential vs. $\text{RE}^{3+}/\text{RE/V}$	
	RE = Nd	RE = Dy ³³	RE = Nd	RE = Dy ³³
$5 \text{ Ni} + \text{RE}^{3+} + 3 \text{ e}^- \rightleftharpoons \text{RENi}_5$	0.95	1.04	0.68	0.71
$3/2 \text{ RENi}_5 + \text{RE}^{3+} + 3 \text{ e}^- \rightleftharpoons 5/2 \text{ RENi}_3$	0.68	0.87	0.41	0.54
$2 \text{ RENi}_3 + \text{RE}^{3+} + 3 \text{ e}^- \rightleftharpoons 3 \text{ RENi}_2$	0.48	0.62	0.21	0.29
$\text{RENi}_2 + \text{RE}^{3+} + 3 \text{ e}^- \rightleftharpoons 2 \text{ RENi}$	—	0.49	—	0.16
$\text{RE}^{3+} + 3 \text{ e}^- \rightleftharpoons \text{RE}$	0.27	0.33	0	0

Table II. Thermodynamic properties of Nd–Ni intermetallic compounds in two-phase coexisting states in this system at 1123 K.

Coexisting state	$\Delta \bar{G}_{\text{Nd}}/\text{kJ}(\text{mol Nd})^{-1}$	$\Delta \bar{G}_{\text{Ni}}/\text{kJ}(\text{mol Ni})^{-1}$
Ni + NdNi ₅	−196.8	0 ^{a)}
NdNi ₅ + NdNi ₃	−118.7	−15.6
NdNi ₃ + NdNi ₂	−60.8	−34.9

a) From the approximation that the activity of Ni is unity at this temperature.

Table III. Standard Gibbs energies of formation for Nd–Ni alloys at 1123 K in per mole atoms.

Phase	$\Delta G_{\text{f}}^{\circ}(\text{Nd–Ni})/\text{kJ mol}^{-1}$	
	This study	CALPHAD[34]
NdNi ₅	−32.8	−22.9
NdNi ₃	−41.4	−28.1
NdNi ₂	−43.5	−31.7

were calculated from a_{Ni} . The calculated values of $\Delta \bar{G}_{\text{Nd}}$ and $\Delta \bar{G}_{\text{Ni}}$ are summarized in Table II. Finally, the standard Gibbs energies of formation for Nd–Ni alloys ($\Delta G_{\text{f}}^{\circ}(\text{Nd–Ni})$) were calculated from $\Delta \bar{G}_{\text{Nd}}$ and $\Delta \bar{G}_{\text{Ni}}$. The obtained values and the reported values³⁴ calculated by CALPHAD technique and WinPhad software are summarized in Table III. Our values are in relatively good agreement with the reported CALPHAD values, but all the values obtained in this study are more negative.

Conclusion

In this study, the electrochemical formation of Nd–Ni alloys was investigated in a molten $\text{CaCl}_2\text{--NdCl}_3$ (1.0 mol%) system at 1123 K. The metallic Nd deposition potential was 0.27 V vs. Ca^{2+}/Ca . After potentiostatic electrolysis of a Ni electrode at 0.30 V for 150 s, three potential plateaus were observed at 0.48, 0.68, and 0.95 V in an open-circuit potentiogram, which suggested three different two-phase coexisting states. SEM, EDX, and XRD analyses confirmed that the thermodynamically stable phases at 0.30, 0.50, 0.80, and 1.00 V are NdNi₂, NdNi₃, NdNi₅, and Ni, respectively. The equilibrium reactions for Nd metal and Nd–Ni alloys and their corresponding potentials were determined. The efficient separation condition for Dy/Nd by DyNi₂ manufacturing was discussed. Based on the potentials, the standard Gibbs energies of formation were calculated and compared with the reported CALPHAD values.

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