Selective Extraction and Recovery of Nd and Dy from Nd-Fe-B Magnet Scrap by Utilizing Molten $MgCl_2$

SAKAE SHIRAYAMA and TORU H. OKABE

Fundamental experiments are conducted with the aim of developing an efficient recycling process for rare earth elements (REEs) from neodymium-iron-boron (Nd-Fe-B) permanent magnet scrap. Molten magnesium dichloride ($MgCl_2$) was chosen as an extraction medium, which can selectively chlorinate and extract REEs in magnet alloys. Dysprosium-containing Nd-Fe-B magnet alloy was immersed in molten $MgCl_2$ at 1273 K (1000 °C) for 3 to 12 hours. The results of the experiments clearly show that the REEs in the magnetic alloy were successfully extracted into the molten salt, while the Fe-B alloy remained in a solid form. The extraction ratios of Nd and Dy were at most 87 and 78 mass pct, respectively. After the extraction experiment, excess $MgCl_2$ and Mg were removed by vacuum distillation and the rare earth chlorides were recovered. Thus, the feasibility of this method for efficient recovery of rare earths using molten $MgCl_2$ is demonstrated.

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I. INTRODUCTION

NEODYMIUM-IRON-BORON (Nd-Fe-B) sintered magnets[1,2] are rare earth permanent magnets, which have extremely high magnetic intensity. When doped with dysprosium (Dy), Nd-Fe-B can sustain its high magnetic intensity even at high temperatures.[3] This feature makes Nd-Fe-B magnets suitable for wider applications, including the fabrication of motors for electronic vehicles (EVs), compressors in air conditioners, and power generators. In response to the increasing demand for these applications, the production of Nd-Fe-B magnets has increased significantly and is expected to increase further. However, Nd and Dy are rare earth elements (REEs) and are therefore difficult to procure. For example, Dy is scarce in the Earth's crust and economically feasible ores of Dy are found only in limited regions (*i.e.*, ion clay ore from the southern part of China). Accordingly, Dy is currently in short supply and is very expensive. Although Nd is rather abundant, radioactive wastes such as uranium (U) and thorium (Th) compounds are always present during the mining and smelting of Nd. In the near future, used magnet scrap discarded from EVs will be an important secondary source of a stable supply of these materials. In order to ensure a reliable supply of valuable REEs and to save energy and natural resources consumed by the production of REEs from ores, it is important to develop an efficient recovery process for Nd and Dy from Dy-containing Nd-Fe-B magnet scrap materials.

Currently, magnet scrap can be classified into two types: those generated during production processes, *e.g.*, alloy fabrication, magnet shaping, and grinding; and those discarded from used industrial products. REEs are usually recovered from scrap produced in magnet manufacturing by a wet process using multistage hydrometallurgical methods that generate a large quantity of waste acid solutions. However, magnets from used industrial products are currently not recycled, with the exception of the large magnets used in medical magnetic resonance imaging (MRI) equipment. The large magnets used in motors for EVs are a good target for recycling, as they are disposed of within 10 years. To recycle a large quantity of magnet scrap, the pyrometallurgical method is advantageous from an environmental perspective. This technique is an alternative to the hydrometallurgical method, which produces a large amount of waste solution, including the very strong oxalic and hydrofluoric acids. In addition, the pyrometallurgical process is relatively simple with a fast processing time, which is suitable for large-scale operation.

In order to develop an environmentally friendly recycling process for REEs with high efficiency, many studies based on pyrometallurgical methods have been carried out for various kinds of magnet scraps.[4–7] Some of the major research works are summarized in Table I.[7–29] Takeda *et al.* demonstrated the direct extraction of Nd from magnet scrap using molten

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Table I. Summary of the Literature Presenting Separation or Recovery Processes for REE based on Dry Processes

Inventor or Author, Reference	Description of the Process	Chemical Reaction / Temperature / Note
Extraction into collector metals		
Yu *et al.*[8]	REE extraction by molten metal	$Nd(\text{in alloy}) + Mg(l) \rightarrow Nd\text{-}Mg(l)$ / 948 K to 978 K (675°C to 705°C)
Takeda *et al.*[9–11]	recovery of Nd from Nd-Fe-B magnet scrap by molten Mg	$Nd + Mg(l) \rightarrow Nd\text{-}Mg(l)$ / 1073 K to 1273 K (800 °C to 1000 °C) / Mg was removed from obtained Nd-Mg alloy by vacuum distillation.
Takeda *et al.*[12]	recovery of Nd from Nd-Fe-B magnet scrap by molten Ag	$Nd + Ag(l) \rightarrow Nd\text{-}Ag$ / 1273 K to 1573 K (1000 °C to 1300 °C) / Nd was recovered from obtained Nd-Ag alloy as Nd_2O_3 by selective oxidation.
Separation by volatilization		
Murase *et al.*[13–15]	REE recovery and separation from RE magnet scrap by chemical vapor transportation (CVT)	$n\ RECl_x(s, l) + (m/2)\ Al_2Cl_6(g) \rightarrow RE_nAl_mCl_{nx+3m}(g)$ / 1323 K (1050 °C) / $AlCl_3$ was reacted with RE chlorides to form complex vapors, $RE_nAl_mCl_{nx+3m}(g)$.
Uda *et al.*[16,17]	separation of RE halide mixture by selective reduction and vacuum distillation	$[RE_{(1)}X_3 + RE_{(2)}X_3\ \text{mixture}] + M(\text{reductant}) \rightarrow [RE_{(1)}X_2 + RE_{(2)}X_3\ \text{mixture}]$ (X = Cl, I) / 950 K (677 °C) / Obtained halides were separated according to the difference in volatility between the di- and trihalides at 1273 K (1000 °C).
Recovery into slag phase		
Saito *et al.*[18–21]	recovery of REE from magnet scrap by glass slag method	$Nd_2Fe_{14}B(l) + B_2O_3(s) \rightarrow Nd_2O_3(\text{slag}) + 3\ Fe_2B(l) + 8\ Fe$ / 1833 K (1560 °C) / Extraction of Sm from Sm-Fe alloy, and extraction of Tb from Tb-Fe alloy were also investigated by authors.
Sekimoto *et al.*[22]	recovery of REE from magnet scrap into $RE_xO_y\text{-}B_2O_3$ slag phase	$RE(\text{in alloy}) + B_2O_3(l) + Fe\text{-}C(l) \rightarrow RE_xO_y\text{-}B_2O_3(\text{slag}) + B_2O_3(\text{slag}) + Fe\text{-}C(l)$ / 1443 K to 1723 K (1170 °C to 1450 °C) / RE_xO_y was enriched in $RE_xO_y\text{-}B_2O_3$ phase under the equilibrium of 3 liquid phases.
Molten salt electrolysis		
Oishi *et al.*[23–25]	recovery of REE from magnet scrap anode by electrolysis using molten salt and an alloy diaphragm	anode: $RE(\text{in magnet alloy}) \rightarrow RE^{3+}(\text{in anolyte}) + 3\ e$, cathode: $RE^{3+}(\text{in catholyte}) + 3\ e \rightarrow RE(s)$ / 723 K (450 °C) / LiCl-KCl was used as molten salt. Transition metal (M) was used as a diaphragm to produce RE-M alloy working as a bipolar electrode. Surface reaction of the bipolar electrode in $LiF\text{-}CaF_2\text{-}NdF_3$ system at 1123 K was also studied by authors.
Selective chlorination		
Itoh *et al.*[26]	recovery of REE from Nd-Fe-B magnet scrap by selective chlorination using NH_4Cl	$RE_2O_3 + 6\ NH_4Cl \rightarrow 2\ RECl_3 + 6NH_3 + 3H_2O$, $m\ (NH_4Cl) + RECl_3 \rightarrow (NH_4)_mRECl_{m+3}$ / 523 K to 623 K (250 °C to 350 °C)
Uda[27]	recovery of REE from magnet sludge by $FeCl_2$	$2\ Nd + 3\ FeCl_2 \rightarrow 3\ Fe + 2\ NdCl_3$ / 1073 K (800 °C) / Excess $FeCl_2$ was separated from RE chlorides by vacuum distillation.
This study[28,29]	recovery of Nd and Dy from Nd-Fe-B magnet scrap utilizing molten salt	$2\ Nd(s) + 3\ MgCl_2(l) \rightarrow 2\ NdCl_3(l) + 3\ Mg(l)$ $Dy(s) + MgCl_2(l) \rightarrow DyCl_2(l) + Mg(l)$ / 1273 K (1000 °C)

metals.[9–12] They also proposed an environmentally sound system in which valuable REEs are recovered from a mixture of different kinds of scraps using magnesium (Mg) scrap as a rare earth extraction medium. Murase *et al.* developed a chemical vapor transportation (CVT) method to separate and recover REEs.[13–15] They treated magnet scrap with aluminum chloride ($AlCl_3$) vapor at high temperatures and the REEs were recovered as vapor complexes, *e.g.*, $REAlCl_3$ (*RE* rare earth). The selective reduction and distillation process proposed by Uda *et al.* is another example of a rare earth separation process involving gas-phase separation.[16,17] Mixed rare earth compounds were converted into halides, and then separated according to the differences in the vapor pressure of species with different oxidation states. Other proposed processes involve rare earth oxidation by molten slag phase,[18–22] molten salt electrolysis,[23–25] and selective chlorination.[26,27] Some of these techniques are feasible for "in-process" (or "in-house") magnet scrap, or scrap supplied by a certain production route with a defined composition. However, in the case of processing large quantities of rare earth magnets from discarded industrial products such as EV batteries, the compositional variations in the magnet alloys themselves as well as contamination by iron (Fe), aluminum (Al), copper (Cu), nickel (Ni), and other metals need to be considered. In this respect, recent studies focus more attention on how to separate rare earth elements from these impurities, and how to separate different kinds of rare earth elements from each other.

The authors aim to develop an efficient recovery process for REEs from relatively large magnet scraps from industrial products. To this end, the authors have proposed a dry process in which REEs are selectively recovered alongside other metals from end products such as EVs.[28,29] Figure 1 shows a flow chart of the recovery process examined in this study, which consists of an extraction step and a separation step. In the extraction step, molten magnesium chloride ($MgCl_2$) was used as an extraction agent to extract and recover the valuable Nd and Dy. By simply immersing magnet scraps into molten $MgCl_2$, the REEs are selectively chlorinated and extracted into molten salt, leaving the Fe-B alloy as a solid phase. In the separation step, vacuum distillation was applied to remove excess $MgCl_2$ and by-product Mg from the mixed salt obtained during the extraction step. Simultaneously, chlorides of Nd and Dy in the mixed salt can be separated from each other using the differences in their vapor pressures. In this process, REEs can be efficiently extracted by solid/liquid reaction, in which both high reaction speed and large mass transfer can easily be achieved. In addition, highly purified rare earth compounds are expected to be obtained through the gas-phase distillation process. Therefore, this process is considered suitable for the recovery of REEs from large amounts of magnet scrap that have variable compositions and contaminant elements. Furthermore, an environmentally sound process can be achieved by recovering and reusing the $MgCl_2$. In this paper, thermodynamic analyses and the results of fundamental experiments are reported and the feasibility of the proposed process is discussed.

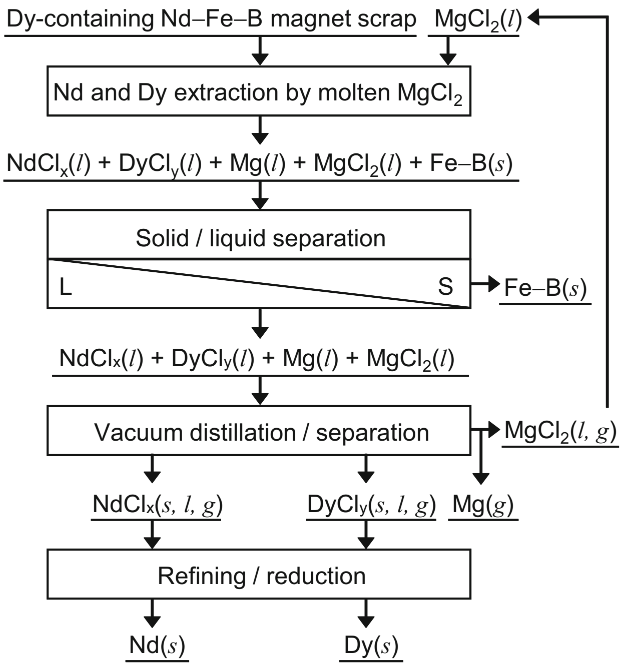

Fig. 1—The new recovery process of REE from Nd-Fe-B magnet scrap by utilizing molten $MgCl_2$ proposed in this study.

II. THERMODYNAMICS

In the first part of this study, the authors investigate a suitable molten salt for the extraction step. In order to selectively extract REE from industrial scrap, metals such as Fe, Al, Cu, and Ni, which account for the main portion of industrial scrap, remain in a solid metal phase. Therefore, the extraction medium needs to be non-reactive with these metals, and reactive with REEs. In addition, it is desirable that the obtained rare earth compounds can be easily recovered using vacuum distillation. In this section, the thermodynamic properties of the elements and compounds related to the process using $MgCl_2$ as an extraction medium are discussed.

Figure 2 shows the standard Gibbs energy of formation for several chlorides as a function of temperature.[30–32] The crosses and filled circles in the figure represent the melting point and boiling point of each compound, respectively. As shown in this Ellingham diagram, Nd and Dy are easily chlorinated by metal chlorides such as $NiCl_2$, CuCl, $FeCl_2$, $ZnCl_2$, BCl_3, $AlCl_3$, and $MgCl_2$, because the formation energy of their chlorides are low. On the other hand, Fe and B are not chlorinated by $AlCl_3$, $MgCl_2$, $DyCl_x$, $NdCl_3$, and NaCl. Therefore, when magnet alloy reacts with $MgCl_2$ at high temperature, only Nd and Dy are expected to be chlorinated by $MgCl_2$, while the main component of the magnet (Fe) and B are not. It is important to note that metals such as Al, Cu, and Ni that often co-exist in industrial scrap, are also not chlorinated by $MgCl_2$. $AlCl_3$ may be another

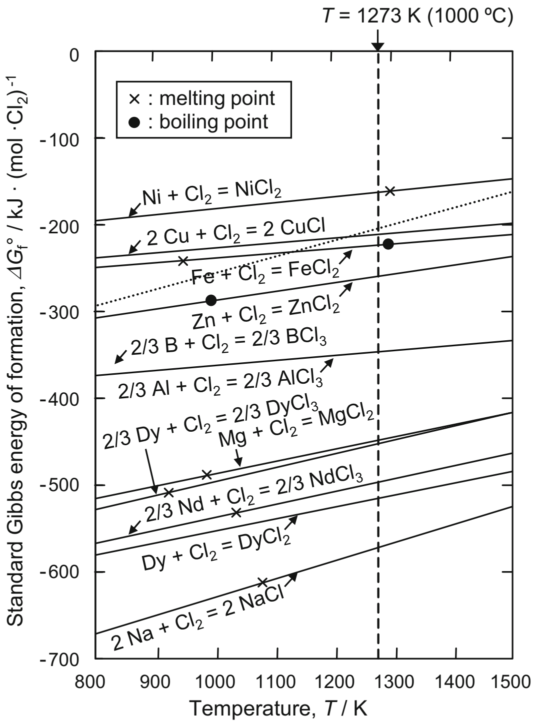

Fig. 2—Standard Gibbs energy of formation for several chlorides. Thermodynamic data in the referenced document and databases[30–32] are plotted.

suitable extraction medium for selective extraction of rare earth elements. However, $MgCl_2$ has the advantage of a faster reaction speed because liquid $MgCl_2$ is stable at higher temperatures than $AlCl_3$, and is able to dissolve chlorinated rare earth elements into the liquid phase and remove them from the surface of the magnet scrap. The reaction temperature of the extraction experiment was set at 1273 K (1000 °C) in order to obtain sufficient chemical and physical reaction speeds.

When magnet alloy is immersed in molten $MgCl_2$, rare earth elements are expected to be extracted into $MgCl_2$ as rare earth chlorides according to reactions [1][30] and [2][30,31] below.

$$2\mathrm{Nd}(s) + 3\mathrm{MgCl_2}(l) \rightarrow 2\mathrm{NdCl_3}(l) + 3\mathrm{Mg}(l) \quad \Delta G^\circ = -\,151.7\ \mathrm{kJ\ at\ 1273\ K\ (1000\ ^\circ C)} \tag{1}$$

$$2\mathrm{Dy}(s) + 3\mathrm{MgCl_2}(l) \rightarrow 2\mathrm{DyCl_3}(l) + 3\mathrm{Mg}(l) \quad \Delta G^\circ = -\,63.5\ \mathrm{kJ\ at\ 1273\ K\ (1000\ ^\circ C)} \tag{2}$$

Assuming that Fe and B remain as a solid phase, the mixed salt containing the rare earth chlorides can be recovered through physical separation from the solid Fe-B alloy. The full extraction reaction of rare earth element from magnet scrap is shown by reaction [3].

$$\mathrm{Dy\text{-}Nd\text{-}Fe\text{-}B}(s) + \mathrm{MgCl_2}(l) \rightarrow \mathrm{NdCl_3}(l) + \mathrm{DyCl_2}(l) + \mathrm{Mg}(l) + \mathrm{Fe\text{-}B}(s) \tag{3}$$

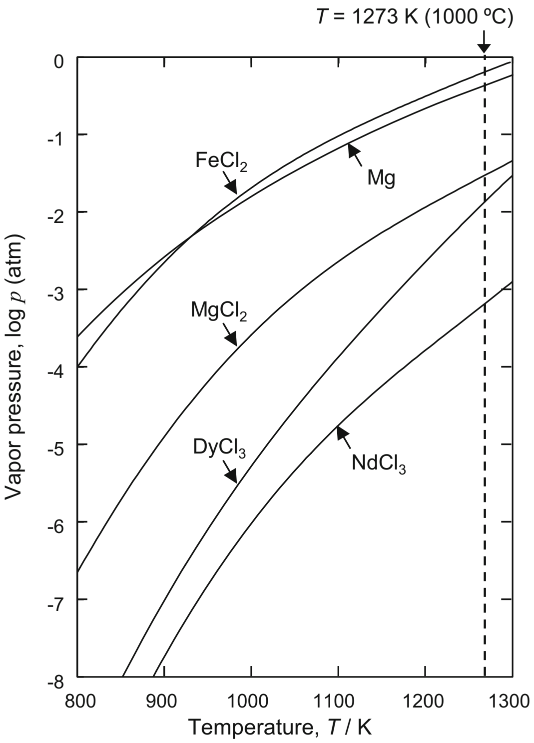

Fig. 3—Vapor pressures of magnesium metal and several chlorides. The vapor pressure for each substance was calculated from standard Gibbs energy of formation in the referenced database.[30]

In this study, vacuum distillation was applied to remove excess $MgCl_2$ and by-product Mg from the mixed salt after the extraction reaction. Figure 3 shows the vapor pressure of Mg metal and several chlorides as a function of temperature.[30] Though $DyCl_2$ is expected to be stable in molten $MgCl_2$ during extraction, there exists few data on the vapor pressure of rare earth di-chlorides. For this reason, vapor pressure of $DyCl_3$ was shown in Figure 3. The vapor pressure of $MgCl_2$ and Mg at 1273 K (1000 °C) is as high as 3.2×10^{-2} atm and 4.6×10^{-2} atm, respectively. Therefore, $MgCl_2$ and Mg are separated from rare earth chlorides that have lower vapor pressures ($p_{\mathrm{NdCl_3}} = 7.9 \times 10^{-4}$ atm, $p_{\mathrm{DyCl_3}} = 1.6 \times 10^{-2}$ atm) by vacuum distillation. Considering that the vapor pressure of rare earth dihalides is lower than that of trihalides by one to two orders of magnitude,[33] separation of $MgCl_2$ and Mg from $DyCl_2$ would be more efficient than that from $DyCl_3$. Furthermore, there is a possibility to recover $NdCl_3$ and $DyCl_2$ separately by taking an advantage of large difference in the vapor pressure of trihalides and dihalides.

III. EXPERIMENTAL PROCEDURES

A. *Extraction of Nd and Dy*

In the extraction experiment, small pieces of rare earth magnet alloy were immersed in molten $MgCl_2$ and the selective extraction of REEs was examined. The materials used in the extraction experiments are shown in Table II. Dy-containing Nd-Fe-B magnet alloy produced by Shin-Etsu Chemical Co., Ltd. was used as simulated magnet scrap. The composition of the alloy

Table II. Materials Used in the Experiments

Materials	Form	Composition / Purity (Mass Percent)	Supplier
Nd-Fe-B Magnet Alloy	small piece	26 pct Nd, 5 pct Dy, 68 pct Fe, 1 pct B*	Shin-Etsu Chemical Co., Ltd.
$MgCl_2$	flake	97 pct up, Anhydrous.	Wako Pure Chemical Industries, Ltd.

*Determined by ICP-AES analysis.

Table III. Experimental Conditions for the Extraction Experiments

Exp. No.	Mass of Nd-Fe-B Magnet Alloy, $w_{\text{Nd-Fe-B}}$ / g	Mass of $MgCl_2$, w_{MgCl_2} / g	Reaction Temperature, T / K (T' /° C)	Reaction Time, t'' / h
1	18.97	26.85	1273 (1000)	3
2	19.87	30.07	1273 (1000)	6
3*	18.69	28.65	1273 (1000)	6
4	14.97	23.21	1273 (1000)	12
5	19.63	31.89	1273 (1000)	12

*Salt recovered after extraction Exp. 3 was applied to vacuum distillation experiment.

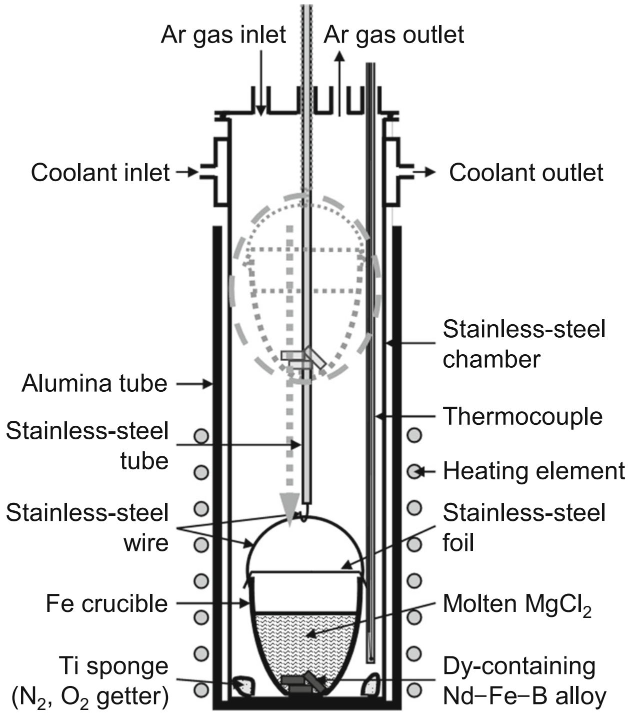

Fig. 4—Schematic illustration of the experimental setup for the extraction experiment using molten $MgCl_2$.

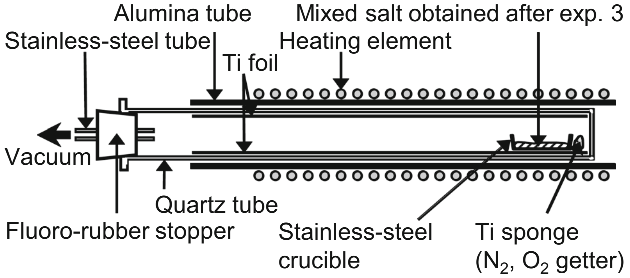

Fig. 5—Schematic illustration of the experimental setup for the recovery experiment based on vacuum distillation.

was 27.4 mass pct Nd, 5.1 mass pct Dy, 66.5 mass pct Fe, and 1.0 mass pct B, according to chemical analyses by inductively coupled plasma atomic emission spectrometry (ICP-AES, Hitachi High-Tech Science Co., SPS4000). The alloy was cut into small pieces (about 5 × 5 × 10 mm) and washed prior to the extraction experiments. The magnet alloy and anhydrous $MgCl_2$ were dried for more than 72 hours in a vacuum dryer (Tokyo Rikakikai Co., Ltd., VOS-201SD) at 423 K (150 °C).

Table III shows the conditions used for the extraction experiments. The weight ratio of magnet alloy to $MgCl_2$ was 2 : 3. Assuming the chlorination reactions [1] and [2] are dominant, the amount of $MgCl_2$ used in these experiments are five times greater than the stoichiometric amount. The reaction temperature, T, was 1273 K (1000 °C), and the reaction time, t'', ranged from 3 to 12 hours. Figure 4 shows the experimental setup for the selective extraction of Nd and Dy from magnet alloy by utilizing molten $MgCl_2$. A stainless-steel reaction tube (100 mm internal diameter, 565 mm length) was set in an electric furnace with a Ti sponge at the bottom as a getter material for oxygen and nitrogen. Magnet alloy and anhydrous $MgCl_2$ were placed in a 100 ml iron crucible and held in the upper section of the reaction tube. The tube was flushed with argon (Ar) gas and the bottom of the tube was heated to 1273 K (1000 °C). Next, the crucible was moved to the bottom of the reaction tube in order to start the extraction reaction by melting the $MgCl_2$ in the crucible. During the experiments, a continuous flow of Ar gas was supplied. After reaction for 3 to 12 hours, the samples were slowly cooled in the furnace and the alloy and the salt in the crucible were recovered.

After the extraction experiments, the chemical phases in the magnet alloy and the salt were identified using X-ray diffraction (XRD, Rigaku Co., RINT 2000). In the XRD analysis, the salts were covered with polyimide film to prevent moisture absorption. The composition of each sample was determined by ICP-AES analysis and the concentration of chlorine was measured using potentiometric titration (DKK-Toa Co., AUT-501). In the ICP-AES analyses, 1000 ppm sample solutions were prepared by dissolving 0.1 g of the samples in mixed acid (96 pct H_2SO_4 : 63 pct HNO_3 : H_2O = 2 : 2 : 10 mL) and diluting it with water to a volume of 100 ml. In the potentiometric titration, 0.1 g of the samples was dissolved in mixed acid (96 pct H_2SO_4 : 63 pct HNO_3 : H_2O = 1 : 1 : 10 mL), and the solution was titrated with 0.01 mol/L $AgNO_3$ solution. A silver/silver chloride electrode ($Ag/AgCl/Cl^-$) was used as a reference electrode to measure the voltage of a silver electrode (Ag/Ag^+) immersed in the sample solution. The concentration of chlorine in the sample solution was calculated from total volume of titrated $AgNO_3$ up to the end of the deposition of AgCl.

B. *Recovery of RE Chlorides*

The recovery experiment was conducted using the mixed salt obtained after the extraction experiment of 6 hours (Exp. 3). In this experiment, excess $MgCl_2$ and by-product Mg in the salt were removed by vacuum distillation, and the rare earth compounds were recovered.

Figure 5 shows the experimental setup for the recovery experiment. A quartz reaction tube (42 mm internal diameter, 46 mm outer diameter, 450 mm length) closed at one end was used as a reaction tube. The mixed salt obtained after Exp. 3 (see Table III) was placed in a stainless-steel crucible (70 mm length, 20 mm width, and 15 mm height) and set in the quartz reaction tube with a Ti sponge as a getter material for oxygen and nitrogen. The inner wall of the reaction tube was covered with a Ti foil so that the depositions after the experiments could be easily recovered. After the reaction tube was flushed with Ar gas, the inside of the reaction tube was evacuated to a total pressure of 2×10^{-4} atm, and the furnace was heated to keep the stainless-steel crucible at 1273 K (1000 °C). The gas pressure was kept lower than 2×10^{-4} atm during vacuum distillation. After vacuum distillation for 6 hours, the reaction tube was slowly cooled in the furnace. Depositions on the Ti foil and the remaining compound in the crucible were recovered and analyzed by XRD, ICP-AES, and potentiometric titration.

IV. RESULTS AND DISCUSSION

A. *Extraction of Nd and Dy*

Photographs of the samples obtained after the extraction experiment (Exp. 1) are shown in Figure 6. The magnet alloy kept its cubic shape and had no obvious

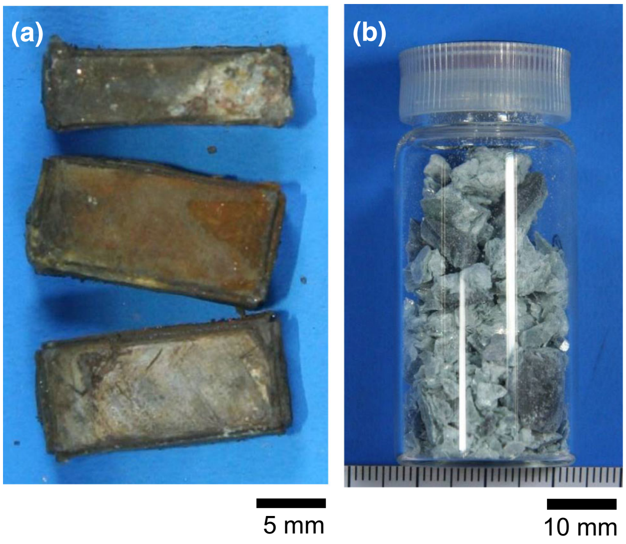

Fig. 6—Photographs of (*a*) the alloy and (*b*) the salt obtained after the extraction experiment using molten $MgCl_2$ at 1273 K (1000 °C) for 3 h (Exp. 1).

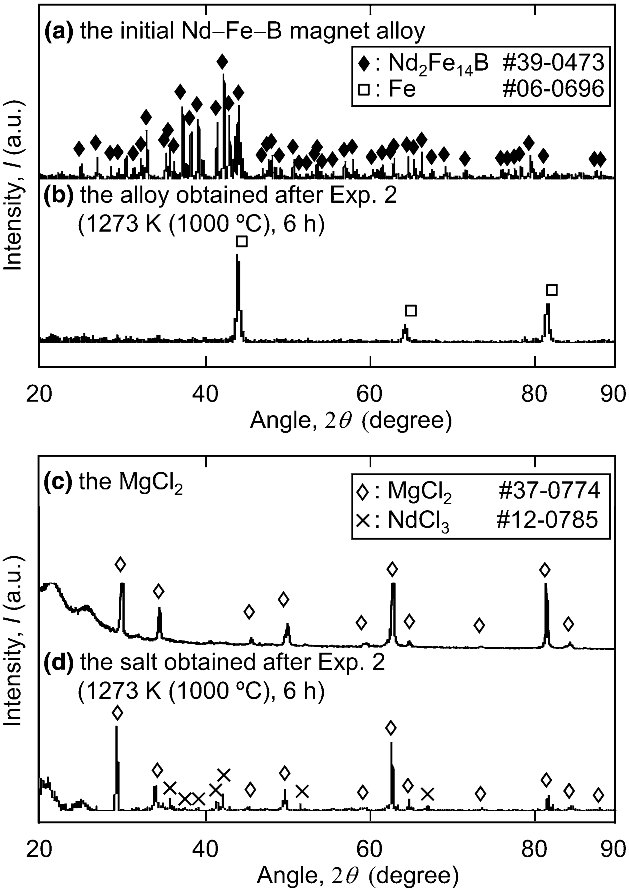

Fig. 7—XRD patterns of the samples in the extraction experiment. (*a*) The initial Nd-Fe-B magnet alloy, (*b*) the alloy obtained after Exp. 2 (1273 K (1000 °C), 6 h), (*c*) the initial $MgCl_2$, and (*d*) the salt obtained after Exp. 2 (1273 K (1000 °C), 6 h).

change in appearance after the treatment. On the other hand, the color of the salt changed from white (the color of the pure $MgCl_2$) to greenish blue.

Figure 7 shows the XRD patterns of samples obtained after the extraction experiment. Results of Exp. 2 are shown for reference. After the extraction experiment, the $Nd_2Fe_{14}B$ phase present in the initial alloy (Figure 7(a)) disappeared, and only the Fe phase was identified in the alloy (Figure 7(b)). The peak positions had shifted slightly towards lower angles compared to the Fe phase PDF #06-0696. As shown in Figure 7(d), the salt contained $NdCl_3$ and $MgCl_2$ phases. These results indicate that Nd in the magnet alloy was extracted into molten $MgCl_2$ as $NdCl_3$ according to reaction [1] during the extraction experiment. No phases containing Dy or B were observed by XRD.

The weights and chemical compositions of the alloy and salt are summarized in Tables IV and V, respectively. Changes in the chemical compositions of the alloy and salt samples lead the authors to the conclusion that Nd and Dy were successfully extracted into the molten $MgCl_2$. The concentrations of Nd and Dy in the magnet alloys decreased with the progress of the reaction, while those in the salts increased. The concentration of Nd in the salt reached 21.3 pct (Exp. 4 in Table V) after 12 hours of reaction time. On the other hand, the relative concentration of Fe and B in the alloys increased compared to the initial values, while those in the salts obtained after the experiments were less than 1.05 mass pct. These data reveal that Fe and B in the magnet alloys remained in the solid phase during the extraction experiments.

The extraction efficiency of the experiment was evaluated from the weight and composition of the samples. The REE extraction ratio, $R_{ex,i}$, is defined by the following formula. The weight of the element i in the samples was calculated from the concentration of i in each sample and the weight of respective samples. The weight percentage of i extracted into the salt compared to that in the initial magnet alloy was calculated.

Table IV. Change in Mass and Composition of the Alloy after the Extraction Experiment

Exp. No.	Reaction Time, t" / h	Mass of Nd-Fe-B Magnet Alloy, $w_{Nd\text{-}Fe\text{-}B}$ / g	Mass of the Alloy after Exp., w_{alloy} / g	Conc. of Element i in the Alloy, C_i (Mass Percent)*					Remaining Ratio of Element i, $R_{re,i}$ (Percent)**	
				C_{Mg}	C_B	C_{Fe}	C_{Nd}	C_{Dy}	$R_{re,Nd}$	$R_{re,Dy}$
Before exp.	—	—	—	< 0.01	1.37	66.7	25.7	4.96	100	100
1	3	18.97	15.93	< 0.01	1.26	86.3	10.0	2.46	32.8	41.7
2	6	19.87	16.45	1.60	1.37	88.1	6.57	2.32	21.2	38.7
3	6	18.69	14.71	1.69	1.30	91.3	4.07	1.61	12.5	25.6
4	12	14.97	11.51	0.72	1.30	93.4	3.69	0.91	11.0	14.1
5	12	19.63	14.58	1.35	1.59	94.5	1.97	0.55	5.7	8.2

*Determined by ICP-AES analysis.

**$R_{re,i}$; Proportion of the weight of element i in the alloy after experiment to the initial weight of element i in the Nd-Fe-B magnet alloy.

$$R_{re,i} = 100 \cdot (w_i,\ \text{in the alloy after exp.})/(w_i, \text{in the initial Nd-Fe-B magnet alloy})\ (\%)$$
$$= 100 \cdot (C_i,\ \text{after exp.}) \cdot w_{alloy}/(C_i, \text{before exp.}) \cdot w_{Nd\text{-}Fe\text{-}B(\%)}.$$

Table V. Change in Mass and Composition of the Salt after the Extraction Experiment

Exp. No.	Reaction Time, t" / h	Mass of $MgCl_2$, w_{MgCl_2} / g	Mass of the Salt after Exp., w_{salt} / g	Conc. of Element i in the Salt, C'_i (Mass Percent)						Extraction Ratio of Element i, $R_{ex,i}$ (Percent)†	
				C'_{Mg}*	C'_B*	C'_{Fe}*	C'_{Nd}*	C'_{Dy}*	C'_{Cl}**	$R_{ex,Nd}$	$R_{ex,Dy}$
Before Exp.	—	—	—	25.3	0.04	0.04	0.02	0.01	75.6	—	—
1	3	26.85	19.78	22.4	0.01	0.78	13.5	2.17	61.1	54.8	45.6
2	6	30.07	30.64	20.1	< 0.01	0.13	14.7	2.02	62.9	88.7	62.8
3	6	28.65	29.12	20.9	< 0.01	0.46	12.8	2.40	63.4	77.6	75.4
4	12	23.21	15.78	15.4	< 0.01	0.26	21.3	3.70	59.4	87.3	78.6
5	12	31.89	20.76	16.5	0.01	1.05	15.6	3.37	63.5	64.1	71.9

*Determined by ICP-AES analysis.

**Determined by potentiometric titration.

†: $R_{ex,i}$; Proportion of the weight of element i in the salt after experiment to the initial weight of element i in the Nd-Fe-B magnet alloy.

$$R_{ex,i} = 100 \cdot (w_i,\ \text{in the salt after exp.})/(w_i,\ \text{in the initial Nd-Fe-B magnet alloy})\ (\%)$$
$$= 100 \cdot (C'_i,\ \text{after exp.}) \cdot w_{alloy}/(C_i,\ \text{before exp.}) \cdot w_{Nd\text{-}Fe\text{-}B(\%)}.$$

$$\text{REE extraction ratio, } R_{\text{ex},i} = \frac{(\text{mass of element } i \text{ in the salt obtained after exp.})}{(\text{mass of element } i \text{ in the initial Nd-Fe-B magnet alloy})} \times 100\ (\text{pct}) = \frac{(C'_i, \text{after exp.}) \cdot w_{\text{salt}}}{(C_i, \text{before exp.}) \cdot w_{\text{Nd-Fe-B}}} \times 100\ (\text{pct}) \qquad [4]$$

where i: Nd or Dy; w_{salt}: mass of the salt obtained after the exp; $w_{\text{Nd-Fe-B}}$: mass of the initial magnet alloy; C'_i,after exp.: conc. of element i in the salt obtained after the exp; C_i,before exp.: conc. of element i in the initial Nd-Fe-B magnet alloy.

Figure 8 shows the REE extraction ratio, $R_{\text{ex},i}$, as a function of the reaction time, t''. The extraction ratio of Nd and Dy increases with the reaction time. After the reaction proceeded for 12 hours, approximately 80 pct of Nd and Dy in the initial magnet alloy was extracted into the molten MgCl_2. Supposing that the produced Mg and RE chlorides are removed from the reaction site by evaporation or dissolution in the liquid MgCl_2, the extraction behavior is considered to be restricted by the diffusion of REEs in the solid magnet alloy. Therefore, the comminution of the magnet alloy before REE extraction process would accelerate the reaction.

The results of the extraction experiments revealed that Nd and Dy in the magnet alloy were selectively extracted directly from the magnet alloy into the molten salt by simply immersing the magnet alloy into molten MgCl_2 at high temperature. The slight shift in the peak position observed in the XRD analysis of the alloy obtained after the extraction experiments may imply that B has dissolved into the solid Fe phase. Although DyCl_2 phases were not observed in the salt sample in the XRD analysis, ICP-AES analysis revealed that the concentration of Dy in the salt was as low as 4 mass pct. This is the primary reason why the authors cannot identify Dy-phases in the salt sample. Since the Mg phase (a by-product of the extraction reaction) was not observed in the salt sample by XRD analysis, it is thought that Mg was removed during the extraction experiment due to the high vapor pressure (4.57×10^{-1} atm) of Mg at 1273 K (1000 °C).

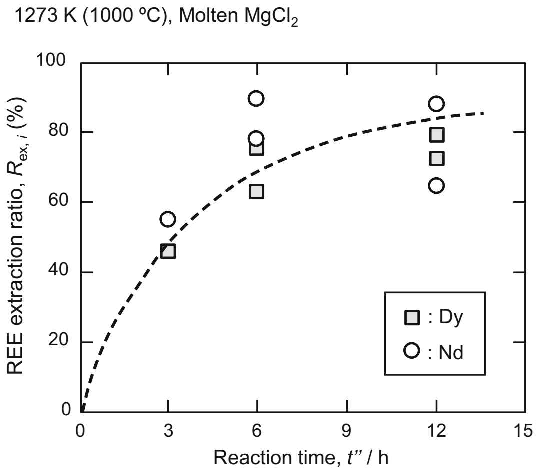

Fig. 8—REE extraction ratio in the extraction experiment.

B. *Recovery of RE Chlorides*

Figure 9(a) shows a photograph of the reaction tube after the recovery experiment by vacuum distillation and an illustration of the temperature distribution in the reaction tube during the recovery experiment. Photographs of the samples obtained at each location described in Figure 9(a) are shown in Figure 9(b). Most of the samples were recovered as a white salt (A) at the section where the temperature during the recovery experiment was 500 K to 900 K (227 °C to 627 °C). The green deposit (B) was recovered at the section where the temperature during the recovery experiment was 1050 K (777 °C), and the black compound (C) remained in the crucible.

Figure 10 shows the XRD patterns of the samples obtained in the recovery experiment. In deposit (A), MgCl_2 phases were observed, with the small peaks identified as the NdCl_3 phase. As shown in Figure 10(c), the NdCl_3 phase was identified in deposit (B) condensed in the high temperature area. The compound (C) that remained in the crucible was identified as NdOCl. These results reveal that it is possible to remove MgCl_2 from the mixed salt after the extraction experiment. Most of the removed MgCl_2 was condensed in the low

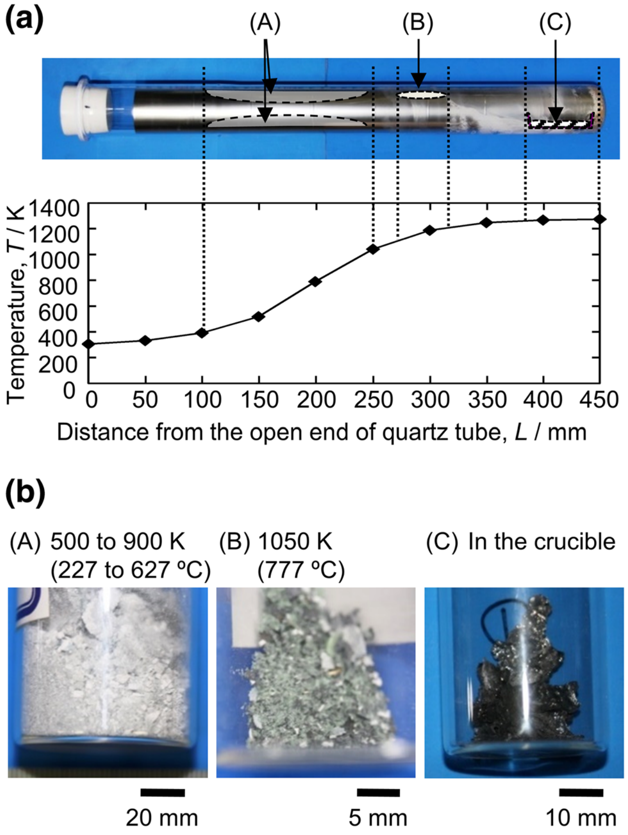

Fig. 9—(*a*) Photograph of the reaction tube after the recovery experiment based on vacuum distillation and the temperature distribution of the tube during the experiment. (*b*) Photographs of the samples obtained at different locations.

temperature area as deposit (A). Nd chlorides were also distilled and condensed with $MgCl_2$ in deposit (B) in the high temperature area closer to the crucible.

The results of the chemical analyses are summarized in Table VI. Except for the compound (C), the summations of the concentrations of the analyzed elements exceeded 95 mass pct. Therefore, Table VI shows the values normalized so that the total is 100 mass pct for those samples. The mixed salt before the recovery experiment contained 12 mass pct of Nd as chlorides, whereas the concentration of Nd in deposit (A) condensed in the low temperature area was reduced to 4 mass pct. On the other hand, deposit (B) and compound (C) with high concentrations of rare earth elements showed a low concentration of Mg, $C''_{Mg} = 0.5$ mass pct. Some small amount of Nd was transported to the low temperature area *via* the gas phase during the recovery experiment, while most of the Dy remained in the crucible. Although the compound (C) was considered to enrich Dy in it, the summation of the analyzed concentrations of each element was less than 50 pct. There may be considerable underestimations of the concentrations of elements (especially for Cl) due to the low solubility of NdOCl or DyOCl into aqueous solutions.

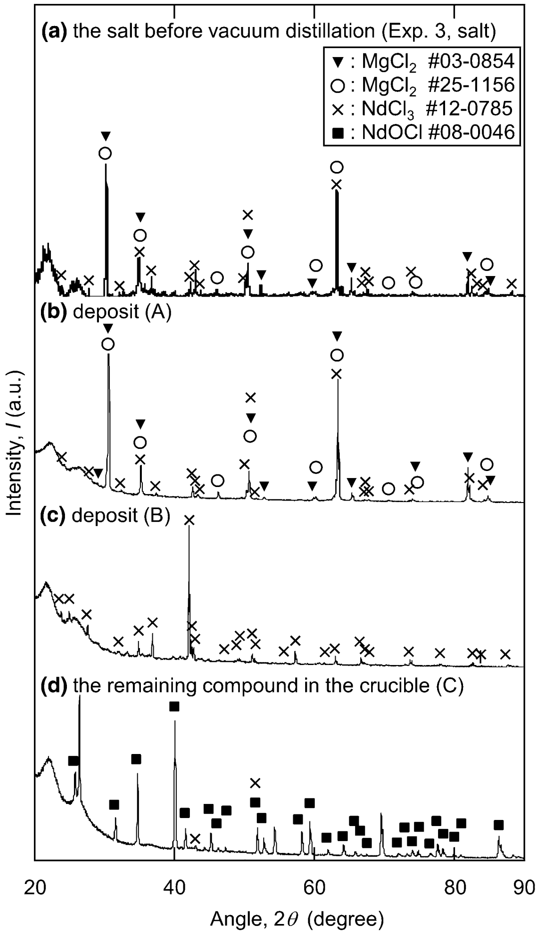

Fig. 10—XRD patterns of the samples in the recovery experiment based on vacuum distillation. (*a*) The salt before vacuum distillation (Exp. 3, salt), (*b*) deposit (A), (*c*) deposit (B), and (*d*) the remaining compound in the crucible (C).

The results of the recovery experiment clearly indicate that excess $MgCl_2$ and by-product Mg can be removed from the mixed salt by vacuum distillation. Part of the $NdCl_3$ in the mixed salt was transported in the gas phase and deposited in the relatively high temperature area as deposit (B). The possibility of refining and separating $NdCl_3$ by utilizing gas-phase transportation was demonstrated. In the recovery experiment, the recovered $MgCl_2$ contained 4.5 mass pct Nd. A higher separation efficiency could be achieved by optimizing the operation conditions such as the vacuum level and temperature distribution. Although some $NdCl_3$ was transported *via* the gas phase, the compound (C) remaining in the crucible was mainly NdOCl. Dy was also detected in compound (C) despite Dy chlorides having a higher vapor pressure than Nd chlorides.

The oxygen contamination in the neodymium chloride may be due to moisture absorption from air during the recovery of the mixed salt after the extraction experiment. Figure 11 shows the chemical potential diagram for the Nd-Cl-O system at 1273 K (1000 °C).[30–32] In this figure, the diagrams for the Dy-O-Cl and Mg-O-Cl systems are also shown for reference. The figure shows that solid NdOCl is chemically stable even under $Mg/MgCl_2/MgO$ equilibrium. The experimental results shown in Figure 10 are consistent with the diagram shown in Figure 11. In this experiment, Dy could remain in the crucible in the form of oxyhalides or oxides when p_{O_2} and p_{Cl_2} were elevated along with the $NdOCl/NdCl_3$ equilibrium. However,

Table VI. Mass and Composition of the Samples Obtained during the Recovery Experiment based on Vacuum Distillation

Sample Name	Mass of Salt before Distillation, w_{salt} / g	Mass of the Deposits after Distillation, $w_{depo.}$ / g	Temp. of the Deposit Location during Distillation, T / K (T' / °C)	Conc. of Element i in the Salt or Deposits, C''_i (Mass Percent)					
				C''_{Mg}**	C''_{B}**	C''_{Fe}**	C''_{Nd}**	C''_{Dy}**	$C''^{\dagger}_{Cl}$
3 (Salt)*	23.46	—	—	20.9	< 0.01	0.46	12.8	2.40	63.4
A	—	17.4	500 to 900 (227 to 627)	24.3	< 0.01	0.03	4.55	0.09	71.0
B	—	1.04	1050 (777)	0.50	< 0.01	0.11	50.8	1.99	46.5
C	—	3.21	1273 (1000)	0.38	< 0.01	1.37	30.3	11.9	0.17

Reaction temperature, T = 1273 K (1000 °C), reaction time, t'' = 6 h.

*Salt obtained after extraction Exp. 3 was used in the recovery exp.

**Determined by ICP-AES analysis.

†Determined by potentiometric titration.

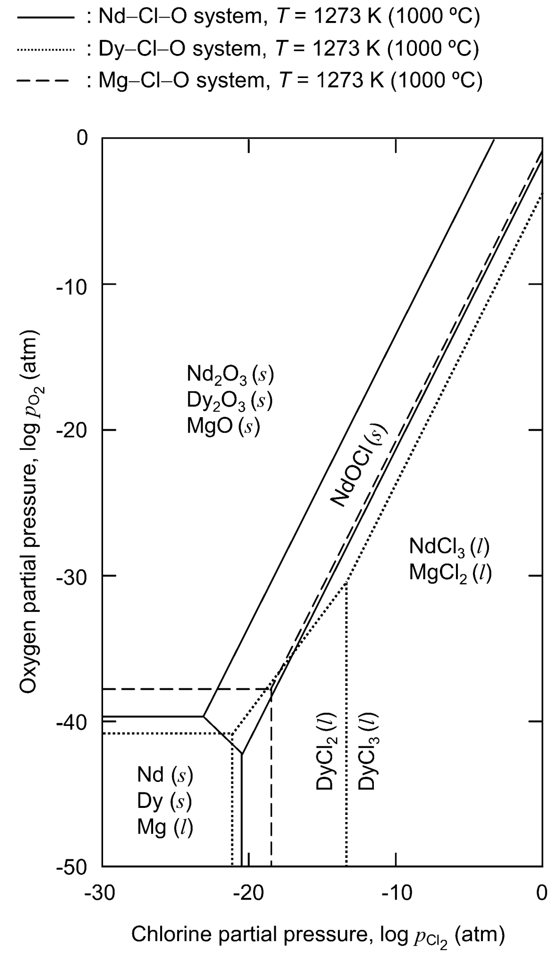

Fig. 11—Chemical potential diagram for the Nd-Cl-O system at 1273 K (1000 °C). The phase equilibria were calculated from standard Gibbs energy of formation in the referenced document and databases[30–32] by assuming activities for all solid and liquid phase were unity.

neither Dy_2O_3 phase nor the DyOCl phase were identified by XRD analysis. Considering the similarity in the chemical properties of Nd and Dy, Dy may replace Nd in the NdOCl phase. Further investigation needs to be conducted in order to understand the behavior and phase of Dy during these experiments.

In order to avoid the formation of NdOCl, oxygen potential should be kept much lower than Mg/MgO equilibrium during recovery of REE salts. Considering that the hydrated rare earth chlorides easily turn into oxyhalides, continuous operation of the extraction and recovery experiments is desirable. For continuous operation, another option of the proposed process is shown in Figure 12. As the authors demonstrated in this study, $MgCl_2$ was a good extractant for the rare earth elements in the magnet scrap. Moreover, vapor $MgCl_2$ was easily transferred and separated from the rare earth compounds by vacuum distillation. Taking advantage of transportability of the vapor chlorides, the proposed process can be adapted to a solid/gas reaction system, in which the scraps with complicated shape can be treated with smaller amount of extractant ($MgCl_2$).

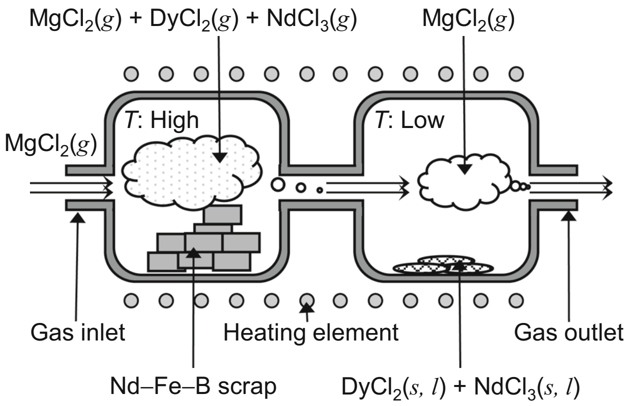

Fig. 12—Concept of a noble recovery process for Nd-Fe-B magnet scrap by utilizing $MgCl_2$ vapor as the extracting agent.

V. CONCLUSIONS

The authors evaluated the feasibility of a process to recover Nd and Dy directly from Nd-Fe-B magnet scrap using $MgCl_2$ as an extraction medium. The experimental equipment for the extraction experiment was designed and constructed. A Dy-containing Nd-Fe-B magnet alloy was immersed in molten $MgCl_2$ for 3 to 12 hours at 1273 K (1000 °C). After 12 hours, approximately 80 pct of the Nd and Dy in the initial magnet sample was successfully extracted into the molten $MgCl_2$. Vacuum distillation under a vapor pressure of 2×10^{-4} atm was conducted on the mixed salt obtained during the extraction experiment. After 3 hours of distillation at 1273 K (1000 °C), excess $MgCl_2$ and by-product Mg were successfully removed from the mixed salt, leaving a deposit containing 50.8 pct Nd and 0.5 pct Mg. The results of the recovery experiments revealed that the extraction medium is easily removed from the salt, leaving behind high purity rare earth chlorides.

In this study, direct extraction and recovery of Nd and Dy from magnet scrap were experimentally demonstrated. The high extraction ratios of the REEs in the extraction experiments demonstrate the suitability of $MgCl_2$ as an extraction medium. Moreover, $MgCl_2$ was removed and the REE chlorides were concentrated by utilizing the differences in vapor pressure. In contrast to the hydrometallurgical process, no part of the process presented here produces any waste water during the concentration of the REEs. The pyrometallurgical process is, in general, suitable for large-scale operation because the reaction speed is fast at elevated temperatures. The authors propose that a large-scale environmentally sound process for the recovery of REEs could be developed using the principles demonstrated in this study.

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