ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

Selective Recovery of Rare Earth Elements from Dy containing NdFeB Magnets by Chlorination

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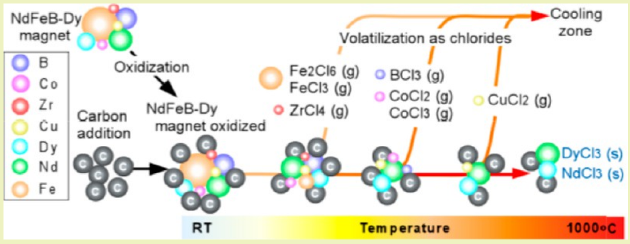

ABSTRACT: To develop an effective recovery process of rare earth metals from Dy containing $Nd_2Fe_{14}B$ magnets (NdFeB-Dy), the release behavior of rare earth metals (Nd and Dy) and coexisting elements (Fe, B, Co, Cu, Zr) from the magnets during chlorination are investigated under the conditions at rate of 30 °C/min and predetermined temperatures from 100 to 1000 °C in a Cl_2 gas stream. Although coexisting elements volatilize from NdFeB-Dy in the low temperature region, Nd and Dy condense in the chlorination residue obtained up to 1000 °C. NdFeB-Dy is preoxidized by heat treatment up 350, 600, and 900 °C in air to represent demagnetized and decarbonized samples. While Fe, Co, and Cu in oxidized sample volatilize during chlorination, Zr and B remain with rare earth metals in the oxidation samples during chlorination temperature up to 1000 °C. When carbon is added to the oxidation samples, all of the elements, except Nd and Dy, volatilize until 1000 °C, thus the rare earth chlorides can be concentrated in the residue after carbochlorination. The rare earth chlorides in the chlorination residues containing carbon can be modified by heat treatment up to 1000 °C under steam to recover rare earth oxides.

KEYWORDS: *NdFeB magnet, Rare earth element, Chlorination, Carbon reduction, Steam modification*

INTRODUCTION

$Nd_2Fe_{14}B$ (NdFeB) magnets have been used in hybrid vehicle (HV) and electric vehicle (EV) motors, nuclear magnetic resonance (NMR), cell phones, home electric appliances, etc. because they have distinct magnetic properties and high intensity. Typically, 5−10 mass % dysprosium (Dy) is added to NdFeB to increase its magnetic anisotropy. NdFeB-Dy can be used for HV or EV motors, because its magnetism is retained at high temperatures. Due to these properties, the demand for and price of NdFeB has recently been rising. With the increase in demand for NdFeB, the price of rare earth elements has also been rising, because rare earth elements such as Nd, Pr, and Dy, which have very low yield globally, are scarce. For these reasons, research and development into low Dy content NdFeB or alternative materials is being conducted, but practical applications will not be available in the immediate future. It is therefore necessary to recover rare earth elements from scrap product to achieve a stable supply. In the NdFeB manufacturing process, 20−30 mass % scrap is generated during the cutting and grinding steps. More than 95% of the cutting and grinding scraps have been recycled in China, but recycling of magnet scrap from manufacturing has been not carried out in Japan due to its high cost.[1] The grinding powder is leached into water and must be transported to a recycling center, because it has high activity and spontaneously combusts. Recycling of magnet scrap from products consists of multiple steps, including separation of the magnets from the product, demagnetization through heat treatment at 300−350 °C, decarbonization (for removal of resin) by combustion at 700−1000 °C under air or oxygen, deoxidization by hydrogen reduction, and remagnetization.[2−4] Several wet processes, acid dissolution,[5] solvent extraction, and the oxalate method[6] are used for recovery of the rare earth elements. These wet chemical methods have poor yield from the acid dissolution and effluent treatment steps, which requires a multiple-step process resulting in high cost. It is important that the recovery process for rare earth elements from NdFeB scrap has as low cost and as few steps as possible, because recovery of the magnets from the product is itself a multistep process.

We previously reported that a combination of oxidation and carbochlorination (simultaneous use of carbon reduction and a chlorination reaction) is an effective method for selective separation of Nd and Pr from NdFeB-Pr.[7] The chlorination method is low-cost, simplifies the overall process, and reduces the amount of effluent requiring treatment as a dry process. However, its disadvantage is that the rare earth elements are recovered as chlorides, and these chlorides have limited application after recovery.[7] Moreover, it was previously unclear whether selective recovery of Dy by chlorination was possible.

The goals of the present study were to elucidate the volatile behavior of rare earth elements and coexisting elements in NdFeB during chlorination, and to investigate the effects of

Received: January 26, 2013
Revised: March 14, 2013
Published: April 19, 2013

Table 1. Composition of NdFeB-Dy Magnet Samples (mass %)

sample	Fe	Nd	B	Dy	Co	Cu	Zr	O^{diff}
NdFeB-Dy	70.6	21.0	1.04	6.3	0.57	0.15	0.33	
NdFeB-Dy-350	55.2	17.0	0.87	5.0	0.45	0.12	0.27	21.1
NdFeB-Dy-600	53.0	16.4	0.81	4.9	0.43	0.11	0.26	24.1
NdFeB-Dy-900	48.6	14.7	0.74	4.5	0.38	0.11	0.24	30.7

temperature, oxidation yield, carbon addition, and holding time on selective recovery of rare earth elements from NdFeB during chlorination. The ability to modify the chlorides obtained after chlorination of NdFeB to oxides was also investigated.

■ EXPERIMENTAL SECTION

NdFeB-Dy magnets were used in the present study. NdFeB-Dy was crushed and sieved to −200 mesh using a stamping mill under an inert atmosphere. The NdFeB-Dy samples were heated to 350, 600, and 900 °C at a rate of 10 °C/min in an air stream with a flow rate of 100 mL-NTP/min. The oxidized samples were then crushed and sieved to −200 mesh again. These oxidized samples were used to represent demagnetized and decarbonized samples and were designated NdFeB-Dy-350, -600, and -900. The weight of NdFeB-Dy increased until the air stream reached 900 °C, as determined by thermogravimetric analysis (TG-DTA2000SA; Burker AXS). The oxidation yields of NdFeB-Dy-350, -600, and -900 were 35, 70, and 100%, respectively, relative to the weight increase of NdFeB-Dy after reaching 1000 °C. Table 1 lists the compositions of the samples. The samples were characterized using a powder X-ray diffractometer (XRD, Ultima IV; Rigaku). After crushing, the samples were loaded into glass sample holders for XRD measurement. Cu Kα radiation was used at a generator setting of 45 kV and 200 mA. The XRD patterns were collected in the 2θ range of 10−80° at a speed of 20°/min and scan step of 0.02°. The XRD peak pattern of NdFeB-Dy was attributed to $Nd_2Fe_{14}B$. The $Nd_2Fe_{14}B$ peaks disappeared in the NdFeB-Dy-350 pattern and formation of Fe_2O_3 was observed. The XRD peaks obtained for NdFeB-Dy-600 and -900 corresponded to Fe_2O_3 and $FeNdO_3$. The oxidation reactions of NdFeB magnets under ambient atmosphere have been reported as follows:[8]

$$2Nd_2Fe_{14}B(s) + 3O_2(g) \rightarrow 24Fe(s) + 2Nd_2O_3(s) + 2Fe_2B(s) \quad (<230\ °C) \tag{1}$$

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad (<500\ °C) \tag{2}$$

$$Fe_2O_3(s) + Nd_2O_3(s) \rightarrow 2FeNdO_3(s) \qquad (<500\ °C) \tag{3}$$

On the basis of the above, NdFeB-Dy-350 should contain Nd_2O_3 in small amounts that would not be detectable by the XRD.

Carbon particles (C 88.3 mass %, H 3.6 mass %, $O^{diff.}$ 8.1 mass %, d_{av} 60.9 μm) derived from phenolphthalein (Nacalai Tesque, G.R.) were used in the chlorination experiment as a reducing agent. Preparation of the carbon particles was carried out in a flow-type fixed-bed quartz reactor. An alumina boat loaded with phenolphthalein was placed at the center of the reactor. The phenolphthalein was heated to 500 °C at a rate of 30 °C/min in a nitrogen stream with a flow rate of 100 mL-NTP/min, and the sample was held at that temperature for 10 min. After heat treatment, the carbon was crushed and sieved to −200 mesh. The carbon particles and oxidized samples were physically mixed at 1:1 by weight.

Chlorination was carried out in a flow-type fixed-bed quartz reactor (i.d. 36 mm, o.d. 40 mm, length 1235 mm).[9,10] Control and monitoring of the reactor temperature was conducted using a thermocouple inserted from out-side the furnace. An alumina boat loaded with 0.2 g of sample was placed at the center of the reactor. The atmosphere in the reactor was substituted with 100 mL-NTP/min nitrogen gas, and the nitrogen stream was then switched to 100 mL-NTP/min chlorine gas (99.4%). The samples were heated at a rate of 30 °C/min to a predetermined temperature (100−1000 °C) in the chlorine gas stream. After selected reaction times of 0, 30, 60, 90, and 120 min, the nitrogen was again switched on, and the reactor was cooled to room temperature. During chlorination, the excess chlorine gas and volatiles were absorbed by a trap containing a sodium hydroxide solution. The solid yield of the samples after chlorination was calculated as follows:

$$\text{yield (mass \%)} = \text{weight of residue after chlorination} / \text{weight of sample before chlorination} \times 100 \tag{4}$$

The percentage of each element released from the samples was calculated as follows:

$$\text{percent released (\%)} = (\text{elemental content before chlorination} - \text{elemental content after chlorination}) / (\text{elemental content before chlorination}) \times 100 \tag{5}$$

The solid residues obtained by carbochlorination at 1000 °C for NdFeB-Dy-900 and NdFeB-Pr-500[7] were used for steam modification of rare earth chlorides. A flow-type fixed-bed quartz reactor (i.d. 36 mm, o.d. 40 mm, length 600 mm) was used. The samples were heated at a rate of 10 °C/min to a predetermined temperature (200−1000 °C) in a steam atmosphere. Steam was provided by 100 mL-NTP/min nitrogen or air as a carrier gas bubbling into a steam generator heated to 110 °C. The tube from the steam generator to the reactor inlet was held at 110 °C using a ribbon heater to prevent water condensation.

The chlorinated or steam modified residues were placed in a Teflon container and completely submerged in a solution containing HCl and HNO_3. The container was placed in a vessel and heated at 140 °C for 3 h. The solution in the container was recovered, and the elemental content in the solution was analyzed with an inductively coupled plasma spectrometer (ICP-OES, SPS3000; Seiko Instruments). The samples were also characterized by XRD. The solid residues obtained before and after steam modification were extracted with distilled water for 1 h at room temperature. The extract residues and solution were recovered by filtration. The extract residue was dissolved by the above method and the rare earth element content in the extract solution and acid dissolution solution were determined by ICP-OES. The carbon content in the samples obtained by chlorination and steam modification were analyzed using a carbon−sulfur analyzer (EMIA-200; Horiba).

■ RESUTLS AND DISCUSSIONS

Effects of Oxidation Yield and Temperature on Volatilization of Elements during Chlorination. Figure 1 illustrates changes in the release of volatile elements from NdFeB-Dy, NdFeB-Dy-350, -600, and -900 with temperature during chlorination. Volatilization of Fe, B, Co, Cu, and Zr from NdFeB-Dy began at 100−200 °C (Figure 1a). The volatile behavior of Fe and Zr were similar with 100% volatilization at 500 °C. Volatilization of B, Cu, and Co increased with an increase in temperature, and 90−100% of these elements have volatilized by 1000 °C. In contrast, volatilization of Dy and Nd at 1000 °C was only about 10%. Percent volatilization of elements at temperatures up to 1000 °C during chlorination increased in the order of Nd < Dy < B < Co < Cu < Zr = Fe. Fe, Co, and Cu also volatilized above 100

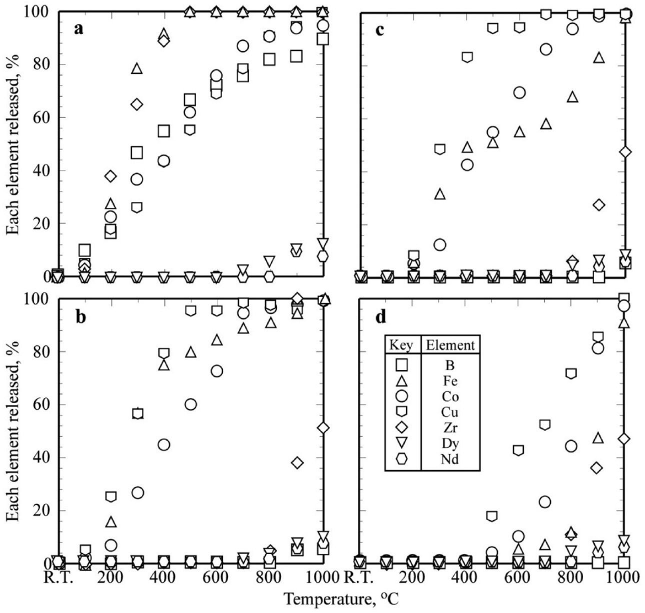

Figure 1. Changes in the volatilization of elements with temperature during chlorination: (a) NdFeB-Dy, (b) NdFeB-Dy-350, (c) NdFeB-Dy-600, and (d) NdFeB-Dy-900.

°C from NdFeB-Dy-350 (Figure 1b). However 75% of Fe had volatilized by 400 °C, its volatilization kinetics slowed at temperatures of 400−1000 °C. On the other hand, >90% of Cu in the solid phase had volatilized by 500 °C. Volatilization of Zr and B began at 800 °C, reaching 50 and 5%, respectively, by 1000 °C. Although the volatilization patterns of B, Fe, Cu, and Zr with temperature in NdFeB-Dy-350 were quite different from those in NdFeB-Dy, volatilization of Nd and Dy were similar to that in NdFeB-Dy. The volatile behavior of elements with temperature, except for Fe, from NdFeB-Dy-600 was similar to those of NdFeB-Dy-350 (Figure 1c). Volatilization of Fe was strong beginning at 200 °C, limited from 400 to 700 °C, then increased again from 700 to 1000 °C. These results suggest that Fe in NdFeB-Dy-600 forms two distinct species. Figure 1d presents the volatilization patterns for elements from NdFeB-Dy-900 with temperature. The volatilization behavior of B, Zr, Nd, and Dy were similar to those in NdFeB-Dy-300 and -600. Volatilization of Co and Cu began above 400 °C and increased with temperature. The initial volatilization temperature of these elements was 200 °C higher than those in NdFeB-Dy-350 and -600. Although volatilization of Fe began at 500 °C, it had reached only 12% by 800 °C. A rapid increase in Fe volatilization occurred above 800 °C, reaching 90% by 1000 °C. Volatilization of the elements from oxidized samples with temperature during chlorination increased in the order of B < Nd < Dy < Zr < Fe < Cu = Co. On the basis of these results, it appears that all elements changed to stable forms that were less affected by chlorination with an increase in the oxidation treatment temperature. The volatilization kinetics of Fe during chlorination decreased with an increase in the oxidation treatment temperature, suggesting strong dependence on the form of Fe present in the oxidation sample. As noted above, in the oxidation samples, Fe was present as Fe_2O_3 and $FeNdO_3$, and the peak intensity of $FeNdO_3$ in XRD increased with increasing oxidation temperature. Therefore, $FeNdO_3$ may be more stable than Fe_2O_3 during chlorination. On the basis of these results, selective separation of Nd and Dy from the other elements in oxidized samples was found to be difficult through chlorination alone.

To investigate volatile forms arising from NdFeB-Dy during chlorination, thermodynamic equilibrium calculations were carried out using HSC (HSC Chemistry for Windows ver. 5.0; Outokumpu Research Oy.). Calculations were performed based on the compositions in Table 1, because $Nd_2Fe_{14}B$ was not available in database. Each element was input as an elemental substance. Figure 2a and b illustrates the results for NdFeB-Dy under a chlorine atmosphere. BCl_3(g) (mp −157 °C, bp 13 °C), $CuCl_2$(g) (mp 573 °C, bp 827 °C), and $ZrCl_4$(g) (sublimation, >300 °C) were identified as the volatile forms of B, Cu, and Zr at a low temperature, to the results shown in Figure 1a. $CoCl_3$(g) and $CoCl_2$(g) (mp 740 °C, bp 1049 °C) were identified as the volatile forms of Co above 300 °C. Although volatilization of B and Cu occurred at lower temperatures in the calculations, volatilization of these elements continued beyond 1000 °C (Figure 1a). It has been reported that B and Cu exist at the grain boundary in NdFeB magnets as $NdCu_2$ and FeNdB,[11] but the HSC database did not contain these compounds. Therefore, differences in the actual and assumed forms of B and Cu likely affected the volatile behaviors of these elements in the calculations. On the basis of the calculation results, Fe is stable as Fe_2Cl_6(g) and $FeCl_3$(g) (mp 304 °C, bp 316 °C) at 100−300 °C and above 300 °C, respectively. Nd and Dy formed $DyCl_3$ and $NdCl_3$, respectively, at low temperatures, and these chlorides volatilized around 600−700 °C as $DyCl_3$(g) (mp 654 °C, b.p 1527 °C) and $NdCl_3$(g) (mp 759 °C, bp 1600 °C) (Figure 2a). However, in the experiments, these rare earth metals did not volatilize (Figure 1a). At present, this difference between the experimental and calculation results has been not clarified. Figure 2c and d presents the results of the HSC calculations for NdFeB-Dy-900 under a chlorine atmosphere. The oxidized compounds input were obtained from the HSC calculations under an air atmosphere based on the compositions in Table 1. Fe_2Cl_6(g) and $FeCl_3$(g) were identified as the volatile forms of

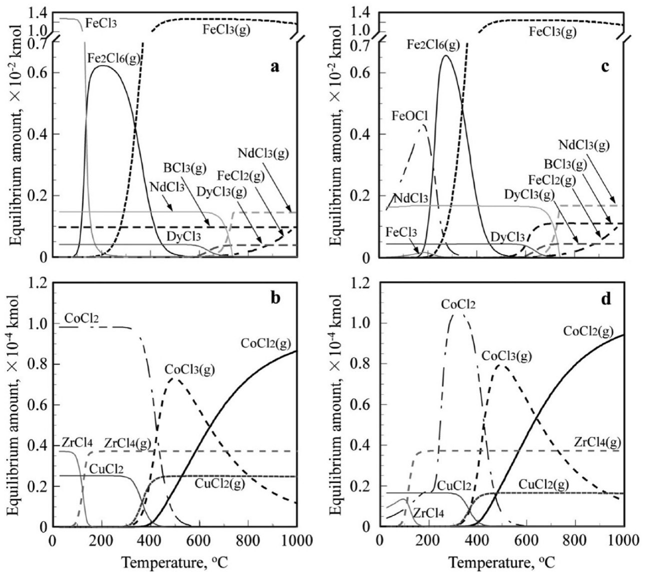

Figure 2. Thermodynamic equilibrium calculations of samples under Cl_2 atmosphere: (a) major elements and (b) coexisting elements in NdFeB-Dy; (c) major elements and (d) coexisting elements in NdFeB-Dy-900.

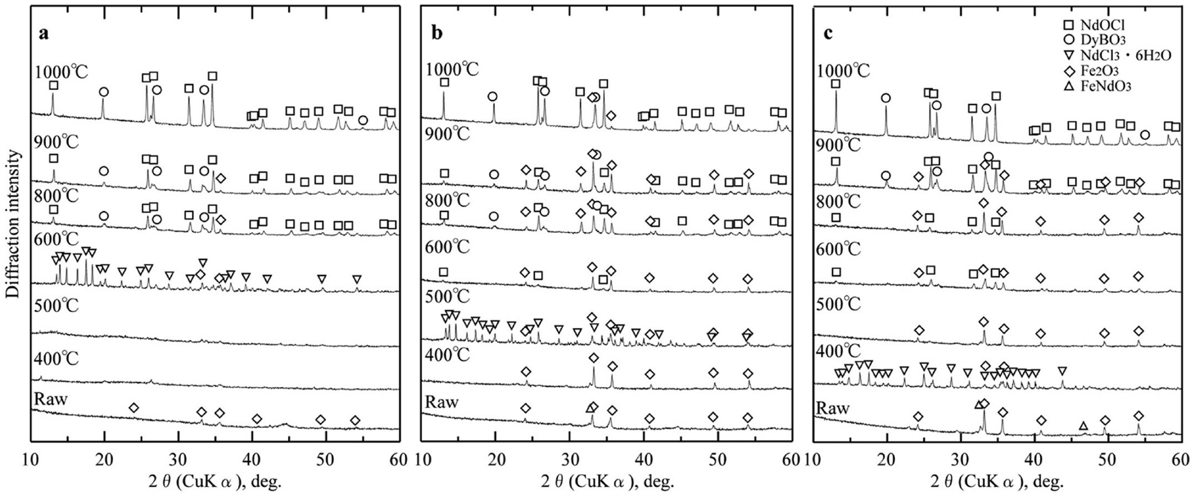

Figure 3. XRD profiles for chlorinated residues obtained at various temperatures: (a) NdFeB-Dy-350, (b) NdFeB-Dy-600, and (c) NdFeB-Dy-900.

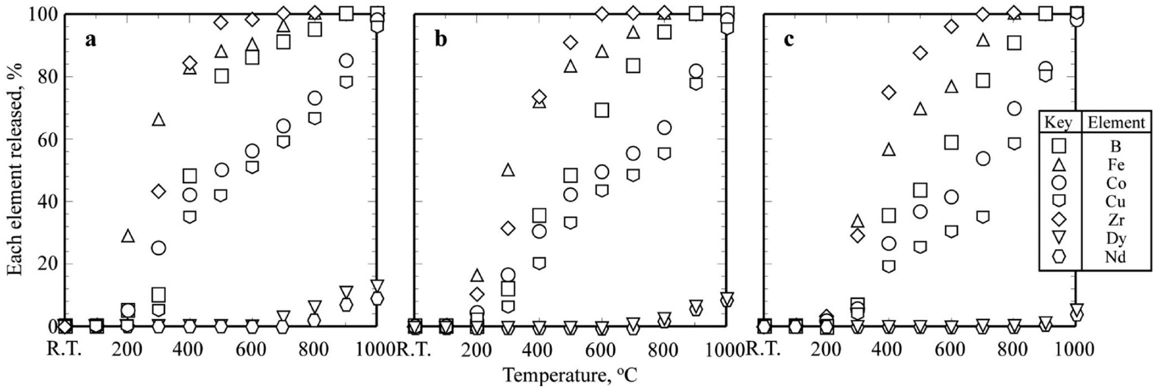

Figure 4. Effects of carbon addition on volatilization of element from samples with temperature during chlorination: (a) NdFeB-Dy-350, (b) NdFeB-Dy-600, and (c) NdFeB-Dy-900.

Fe through FeOCl formation at low temperatures. The volatilization kinetics of Fe decreased with an increase in oxidation treatment temperature (Figure 1b–d) depending on the chlorination reaction through FeOCl formation. Although the calculation results for Co, Cu, and Zr (Figure 2d) were similar to those shown Figure 2a and b, their volatile behavior (Figure 1b–d) differed from the calculation results. These differences may arise from formation of oxidized compounds that are not contained in the HSC database.

To clarify the chlorination reactions of NdFeB-Dy, XRD measurements were carried out on the residues obtained after chlorination of each sample. Figure 3 shows the changes in the XRD patterns of residues obtained from chlorination of NdFeB-Dy-350, -600, and -900. In NdFeB-Dy-350, $NdCl_3 \cdot 6H_2O$ was found in the residue at 600 °C (Figure 3a). Hydration may have occurred during preparation of the XRD measurement sample, because rare earth chlorides have a deliquescent property. The $NdCl_3 \cdot 6H_2O$ peak had disappeared by 800 °C; meanwhile, peaks for $DyBO_3$ and NdOCl appeared at 800 °C, indicating that $NdCl_3$ formed NdOCl. These results suggest that solid–solid reactions may occur between oxidation compounds of coexisting elements remaining in the solid phase and $NdCl_3$ generated during chlorination, with the chlorine in $NdCl_3$ supplied to coexisting oxides. Formation of $NdCl_3 \cdot 6H_2O$ was also found at 500 and 400 °C in NdFeB-Dy-600 and -900 chlorination residues, respectively, (Figure 3b and c). NdOCl was detected above 600 °C in both oxidation samples. These formation temperatures for rare earth element chlorides and oxy-chlorides were shifted to lower temperatures by 100–200 °C compared to those in NdFeB-Dy-350. This temperature shift may be due to structural relaxation of NdFeB-Dy with an increase in the oxidation temperature, increasing contact efficiency between the chlorine gas and Nd in the samples. Thus, rare earth elements and B were stable in the solid phase as NdOCl and $DyBO_3$ during chlorination up to 1000 °C. In addition, it was observed that oxidation treatment promotes initial chlorination reaction of rare earth elements.

Effects of Carbon Addition on Volatile Behaviors of Elements during Chlorination. Figure 4 shows changes with temperature in volatilization of the elements from the oxidized samples during carbochlorination. Although B was stable in the oxidized samples (Figure 1b–d), volatilization began at 200 °C with carbon addition. In all oxidized samples with carbon addition, 100% B volatilization was achieved by 900 °C. Volatilization of Fe did not show the differences observed in the oxidized samples and increased substantially beginning at 100–400 °C in all oxidized samples with carbon addition. Volatilization of Fe from all samples increased with increasing temperature and reached 100% by 800 °C. The same tendencies were found for Co and Cu; these elements had completely volatilized in samples with carbon addition by 1000 °C. The volatilization kinetics of Fe, Co, and Cu increased in the order of NdFeB-Dy-900 < -600 < -350. In the oxidized samples (Figure 1b−d) volatilization of Zr was ∼50% from 700 to 1000 °C in all oxidized samples. In contrast, with carbon addition, Zr quickly volatilized above 200 °C in all samples, reaching 100% by 700 °C (Figure 4). The volatilization behavior of B, Fe, Co, Cu, and Zr from the solid phase with carbon addition was quite different from those in the oxidized samples. However, similar to the oxidized samples, no volatilization of Nd and Dy occurred from the carbon addition samples.

To identify volatile forms during carbochlorination, thermodynamic equilibrium calculations were carried out carbon addition to the oxidized compounds (Figure 3c and d). The volatile behavior of B, Fe, Nd, and Dy, which are the primary components of NdFeB-Dy, and Cu were quite similar to those of the oxidized samples (Figure 2a and b), and $Fe_2Cl_6(g)$, $FeCl_3(g)$, $FeCl_2(g)$, and $BCl_3(g)$ were indentified as the volatile forms. $ZrCl_4(g)$ volatilized between 100 and 500 °C through $ZrCl_4$ formation below 200 °C in the calculation results. On the other hand, Co was stable as $Co_2(CO)_3$ from room temperature in the carbon addition system in the equilibrium calculation results. Because volatilization of Co during carbochlorination was observed (Figure 4), Co likely volatilizes as $CoCl_3(g)$ or $CoCl_2(g)$ as determined in Figure 2b.

XRD analyses of the carbochlorination residues obtained at each temperature were carried out to clarify the carbochlorination reactions. The Fe_2O_3 peak disappeared from the XRD pattern of the NdFeB-Dy-350 carbochlorination residue obtained at 100 °C and only the peak for $NdCl_3{\cdot}6H_2O$ was found in the residue by 200 °C. The peak intensities of Fe_2O_3 and $FeNdO_3$ in NdFeB-Dy-600 and -900 decreased between 100 and 200 °C; by 300 °C, the primary peaks were attributed to $NdCl_3{\cdot}6H_2O$. The $NdCl_3{\cdot}6H_2O$ peak in the carbochlorination residues was found from 200−300 and 1000 °C, and formation of other compounds was not observed. Although the peak of Dy compound was not detectable in carbochlorination residue obtained up to 200−1000 °C by XRD measurement, Dy remains in carbochlorination residue obtained up to 1000 °C as seen in Figure 4. It may cause that Dy content in residue is smaller than that of Nd. On the basis of these results, both carbon reduction and chlorination reactions occur below 100−200 °C.

Changes in the carbon content with temperature during carbochlorination are shown in Figure 5. The carbon content in all samples greatly decreased from 100 to 200 °C. Because volatilization of Fe, the primary component of NdFeB-Dy, began at this temperature (Figure 4), the decrease in carbon likely mainly occurred due to reduction of Fe. The carbon content of NdFeB-Dy-350, -600, and -900 during carbochlorination had decreased by up to 40−50 mass % by 1000 °C. Thus, carbochlorination is an efficient method for selective recovery of rare earth elements from oxidized NdFeB-Dy, because the other elements that compose NdFeB-Dy magnets, volatilize from the solid phase, and only the rare earth elements remain in the residue after chlorination. In addition, we found that the required amount of carbon additive for selective separation of rare earth elements was ≥50 mass % for oxidized NdFeB-Dy.

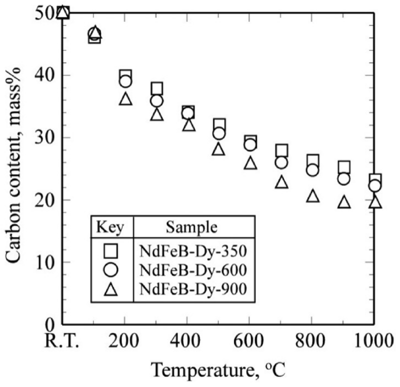

Figure 5. Change in carbon content with temperature during carbochlorination.

It has been reported that carbochlorination occurs as follows:[12]

$$Me_xO_y + xz/2Cl_2 + yC \leftrightarrow xMeCl_z + yCO \tag{6}$$

where Me is the metal, x and y are stoichiometric efficiencies, and z is the valence. On the basis of eq 6 and our experimental results and equilibrium calculations, volatilization of Fe and Nd, the main components of NdFeB-Dy, occurs during carbochlorination up to 1000 °C as follows:

$$Fe_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow Fe_2Cl_6(g) + 3CO(g) \quad (100-600\ ^\circ C) \tag{7}$$

$$Fe_2O_3(s) + 3C(s) + 3Cl_2(g) \rightarrow 2FeCl_3(g) + 3CO(g) \quad (200-1000\ ^\circ C) \tag{8}$$

$$Fe_2O_3(s) + 3C(s) + 2Cl_2(g) \rightarrow 2FeCl_2(g) + 3CO(g) \quad (600-1000\ ^\circ C) \tag{9}$$

$$FeNdO_3(s) + 3C(s) + 3Cl_2(g) \rightarrow FeCl_3(g) + NdCl_3(s) + 3CO(g) \quad (100-400\ ^\circ C) \tag{10}$$

$$2FeNdO_3(s) + 3C(s) + 3Cl_2(g) \rightarrow Fe_2O_3(s) + 2NdCl_3(s) + 3CO(g) \quad (100-400\ ^\circ C) \tag{11}$$

$$Nd_2O_3(g) + 3C(g) + 3Cl_2(g) \rightarrow 2NdCl_3(s) + 3CO(g) \quad (>200\ ^\circ C) \tag{12}$$

Moreover, $DyBO_3$ was found by XRD in residue obtained after chlorination of the oxidized samples up to 800 °C (Figure 3). Appearance of the $DyBO_3$ peak results from volatilization of coexisting elements during chlorination of the oxidized sample, suggesting that a reaction occurs between B and Dy to form a complex compound during oxidation. Thus, eq 13 may occur up to 900 °C during carbochlorination, because volatilization of B occurs up until 900 °C:

$$DyBO_3(s) + 3C(s) + 3Cl_2(g) \rightarrow DyCl_3(s) + BCl_3(g) + 3CO(g) \quad (200-900\ ^\circ C) \tag{13}$$

Effects of Holding Time on Volatilization of Elements during Carbochlorination. Figure 6 presents changes in volatilization of the elements from NdFeB-Dy-900 for various holding times at 700, 800, and 900 °C. Fe volatilization of 100% was achieved by 30 min. Volatilization of Cu and B from the solid phase proceeded rapidly up to 30 min, but no changes were observed above 30 min. Volatilization of Co was 15% by

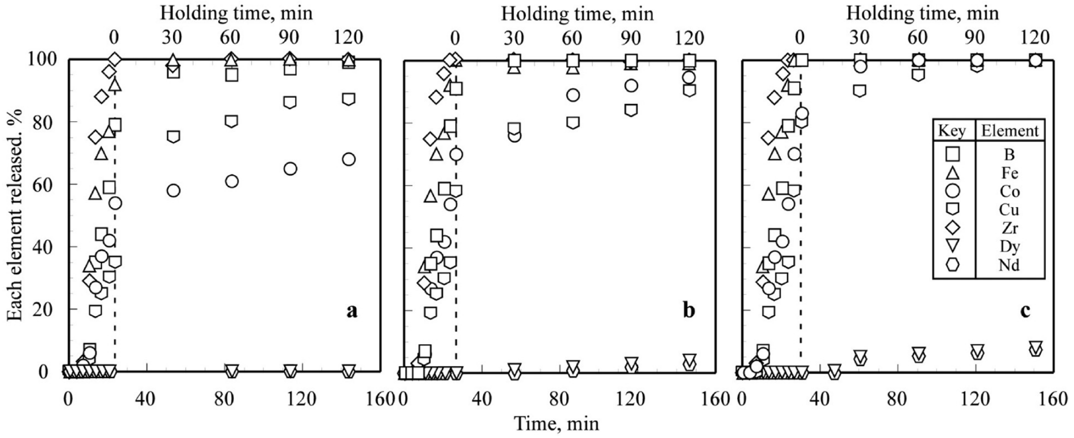

Figure 6. Effects of holding time and temperature on volatilization of elements from samples with carbon addition during chlorination: (a) 700, (b) 800, and (c) 900 °C.

120 min, and the rare earth elements did not volatilize. The magnitude of the holding time effect was Nd = Dy = Co = B = Fe < Cu < Zr. This trend was similar for NdFeB-Dy-350 and -600. Figure 6b shows changes in volatilization of the elements during carbochlorination at 800 °C with holding time. B was 100% volatilized at 30 min, and volatilization of Cu and Co increased with an increase in the holding time, up to 90 and 95%, respectively, at 120 min. Although Nd and Dy had not volatilized at all by 120 min in NdFeB-Dy-900, 4–7% of these elements volatilized from NdFeB-Dy-350 and 600 by 120 min. At 900 °C (Figure 6c), Co and Cu had completely volatilized by 60 and 90 min, respectively. The extent of rare earth elements volatilization from NdFeB-Dy-350 and -600 by 120 min was 16–20 and 10–12%, respectively, with volatilization increasing with decreasing oxidation treatment temperature. When the three oxidized samples were held in chlorine gas at 1000 °C, 100% volatilization of coexisting elements was obtained by 30 min. However, volatilization of rare earth elements also increased with increasing holding time to 4–16% and 16–22% at 30 and 120 min, respectively. Volatilization of Dy was higher than that of Nd. Thus, selective separation of rare earth elements from oxidized samples with carbon addition is possible by holding the samples at 900 °C, because the rare earth elements remain in the carbochlorination residue.

Production of Rare Earth Element Oxides from Carbochlorination Residues by Steam Modification. Figure 7 presents changes in the water-soluble fraction of NdFeB-Dy-900 residues obtained through carbochlorination at 1000 °C by steam modification using nitrogen or air as a carrier gas. The rare earth elements in the carbochlorination residue of NdFeB-Dy-900 obtained at 1000 °C were in the form of chlorides, because they were not found in the dissolved solution of water-treated residues at room temperature. Water-soluble Dy and Nd in steam modified residues greatly decreased above 200 °C and disappeared at 800 °C for both carrier gases (Figure 7). Similar results were found for NdFeB-Pr-500 carbochlorination residues. No volatilization of the rare earth elements was observed up to 1000 °C under either atmosphere.

To clarify changes in the rare earth chlorides, XRD was conducted on the residues after steam modification at each temperature. Figure 8 shows changes in the XRD patterns for the NdFeB-Pr-500 carbochlorination residue during stream modification. NdOCl was identified at 800 °C, and Nd_2O_3 (hexagonal or cubic) was identified at ~900 °C under a steam–nitrogen atmosphere (Figure 8a). Under a steam–air atmosphere (Figure 8b), formation of NdOCl began at 600 °C and Nd_2O_3 (hexagonal or cubic) and Pr oxides were found above 800 °C. Figure 9 illustrates changes in the XRD patterns of NdFeB-Dy-900 carbochlorination residue during steam modification. Under both atmospheres, NdOCl peaks appeared between 600 and 700 °C, changing to Nd_2O_3 (cubic) at 800 °C. $DyNdO_3$ formed up to 900 °C, and Nd_2O_3 (cubic) and $DyNdO_3$ were dominant in the modified residues obtained at 1000 °C under both atmospheres.

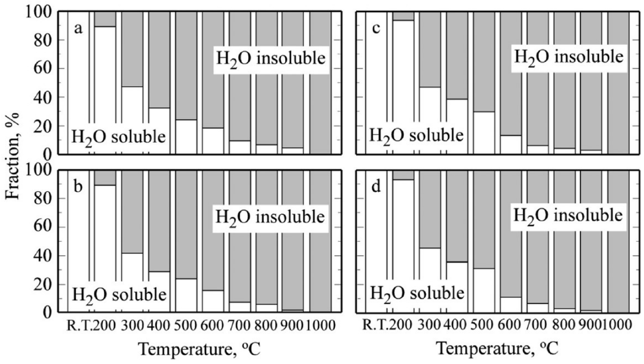

Figure 7. Changes in elemental composition of NdFeB-Dy-900 carbochlorination residue with temperature during steam modification under H_2O–N_2 or air atmosphere: (a) neodymium and (b) dysprosium under H_2O–N_2 atmosphere; (c) neodymium and (d) dysprosium under H_2O–air atmosphere.

To clarify the effect of stream on these changes, XRD measurements were carried out on NdFeB-Pr-500 carbochlorination residues after heat treatment under either the nitrogen or air stream. NdOCl peaks were identified in the residue at 400 °C under both nitrogen and air and remained up to 1000 °C. Pr oxides were found in the residue only under air atmosphere. It has been reported that $NdCl_3 \cdot 6H_2O$, $DyCl_3 \cdot 6H_2O$, and $PrCl_3 \cdot 7H_2O$ are converted to oxy-chlorides and HCl gas up to 400 °C in air through dehydration and dechlorination reactions.[13] Thus, in our experiment, the dechlorination reaction occurs only through dehydration to form oxy-chlorides and HCl gas. These results suggest that the steam affects dechlorination reaction of NdOCl above 800 °C, because only NdOCl was stable in heat treatment under the nitrogen or air stream. Thus, it was determined that the water-

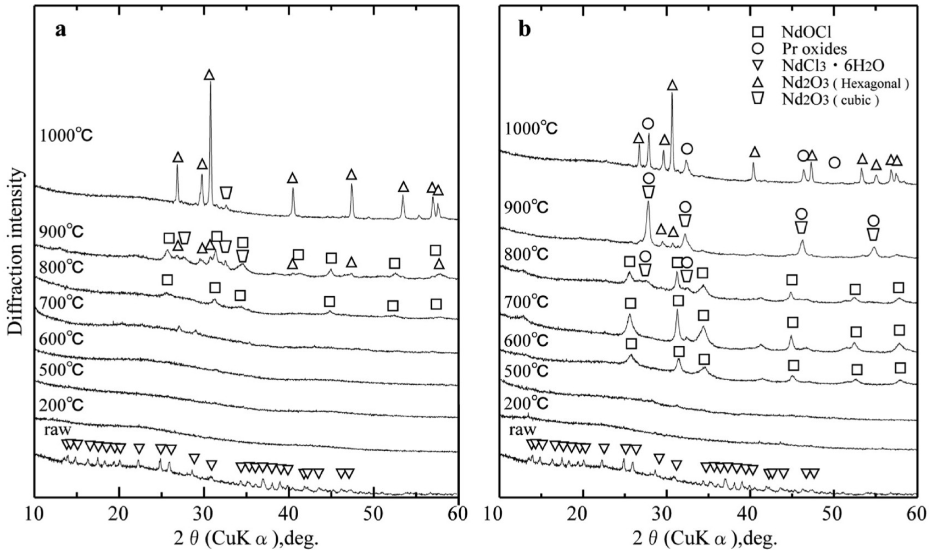

Figure 8. XRD profiles for NdFeB-Pr-500 carbochlorination residues obtained at various temperatures during steam modification under (a) H_2O-N_2 and (b) H_2O−air atmosphere.

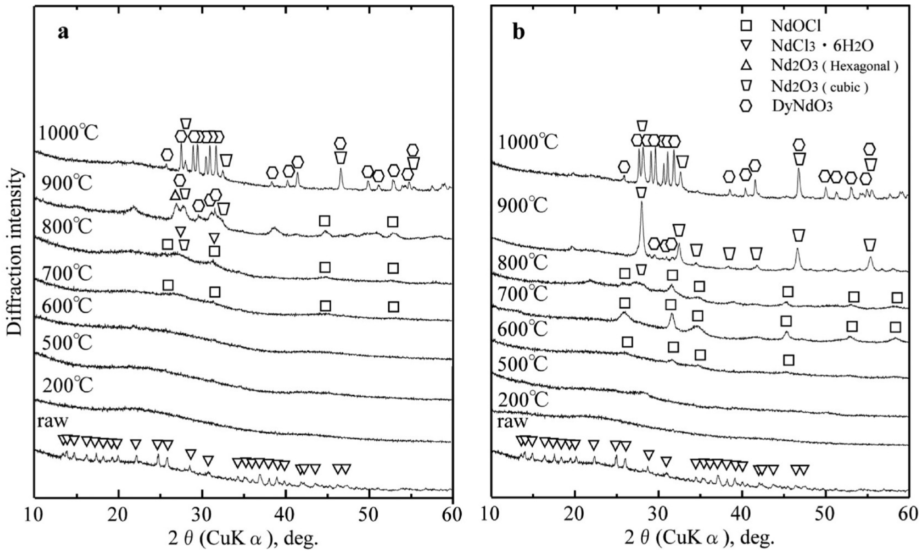

Figure 9. XRD profiles for NdFeB-Dy-900 carbochlorination residues obtained at various temperatures during modification under (a) H_2O-N_2 and (b) H_2O−air atmosphere.

insoluble fraction formed up to 800 °C (Figure 7) consists of oxy-chlorides (NdOCl, PrOCl, or DyOCl) and that rare earth complex oxides are generated above 900 °C as follows:

$$MCl_3{\cdot}nH_2O(s) \rightarrow MCl_3(s) + nH_2O(g) \qquad (<250\ °C) \qquad (14)$$

$$MCl_3(s) + H_2O(g) \rightarrow MOCl + 2HCl(g) \quad (200-800\ °C) \qquad (15)$$

$$2MOCl(s) + H_2O(g) \rightarrow M_2O_3(s) \text{ or Pr oxide}(s) + 2HCl(g) \quad (700-900\ °C) \qquad (16)$$

$$Nd_2O_3(s) + Dy_2O_3(s) \rightarrow 2DyNdO_3(s) \quad (800-1000\ °C) \qquad (17)$$

where M is a rare earth element and n is stoichiometric coefficient.

The change in carbon content in the residues during steam modification is shown in Figure 10. The carbon content of 42 mass % in the carbochlorination residue decreased with an increase in the temperature and was reduced to below the limit of detection of the CS analyzer by 1000 or 800 °C in nitrogen or air carrier gas, respectively. These results demonstrate that steam modification is effective in converting rare earth chlorides in carbochlorination residues to oxides and air is more efficient than nitrogen for use as a carrier gas. In addition, steam modification is possible for carbon reduction.

■ CONCLUSIONS

The present study aimed to achieve efficient and selective recovery of rare earth elements from Dy containing NdFeB magnets (NdFeB-Dy) by carbochlorination. The volatile behavior of NdFeB-Dy elements during chlorination was

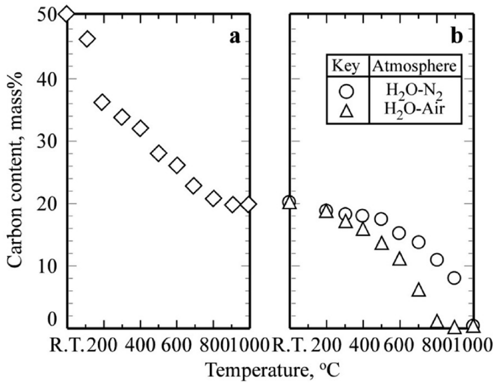

Figure 10. Change in carbon content with temperature during carbochlorination of (a) NdFeB-Dy-900 and (b) with H_2O-N_2 or air modification of NdFeB-Dy-900 carbochlorination residue.

investigated. Nd and Dy condensed into the solid phase during chlorination of NdFeB-Dy and in samples oxidized at 350, 600, and 900 °C (NdFeB-Dy-350, -600, and -900) under air atmosphere before chlorination treatment. Although volatilization of coexisting elements (Fe, Co, Cu, B, Zr) in NdFeB-Dy increased with an increase in temperature during chlorination, B and Zr remained in the solid phase with the rare earth chlorides in oxidized samples. The coexisting elements were able to be completely volatilized, with only Nd and Dy condensed into the solid phase after carbochlorination of the oxidized samples. Holding for up to 120 min at 900 °C was effective for selective volatilization of coexisting elements from the solid phase with carbon addition during chlorination. The Nd and Dy chlorides remaining in the carbochlorination residue were modified to rare earth oxides through steam treatment at 900−1000 °C.

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Notes

The authors declare no competing financial interest.

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