Extraction of Rare Earth Elements from Nd–Fe–B Magnet Scraps by NH_4Cl

Masahiro Itoh, Koji Miura, and Ken-ichi Machida
Center for Advanced Science and Innovation, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871

(Received November 22, 2007; CL-071298; E-mail: machida@casi.osaka-u.ac.jp)

Extraction of rare earth elements from the Nd–Fe–B magnet scraps through the chlorination with NH_4Cl was performed to study the effective process for reusing metal iron as well as rare earths. The $Nd_2Fe_{14}B$ primary phase was selectively converted to neodymium chloride in the yield of ca. 90%, together with α-Fe and Fe–B residue on the basis of the higher chlorine affinity of rare earths.

Since the intermetallic compound of $Nd_2Fe_{14}B$ was developed as the highest performance permanent magnets, it has been used in various application fields for the excellent magnetic properties.[1] Particularly, the annual production amount of Nd–Fe–B sintered magnets has became more than 30000 ton all over the world. However, about 30% of such magnets are produced as solid or powder scraps in the manufacturing processes, e.g. pressing, sintering, cutting, and polishing. Among them, the powder scrap which is essentially generated in the cutting and polishing processes to fit demand size for applications products. Consequently, efficient recycling or reusing processes are strongly demanded for the effective utilization of valuable rare earth elements.

In an industrial scale, the rare earth components of powder scraps are currently recovered by solution processes followed by ion exchange or solvent extraction,[2,3] although these processes involve the generation of much industrial drainages. The other several dry processes proposed for them have not yet met the industrial requirements,[4–8] but the chemical vapor transport method based on metal chlorination[6–8] allows us to recover the rare earth elements from such powder scraps, and furthermore, they are mutually separated from one another by the stability difference of such metal chloride vapor complexes. However, all components of the rare earth and transition metal such as Nd, Fe, B, and the other additives (Pr, Dy, Co, Cu, and so on) are chlorinated, so that the useless chlorides other rare earth ones are also produced.

In this study, the selective chlorination method using NH_4Cl was applied to the powder scrap of Nd–Fe–B sintered magnets to separate Nd element as $NdCl_3$ from Fe-based metallic solid residues. The feasibility as the recycling process for Nd–Fe–B sintered magnet scraps was evaluated and the magnetic properties of the solid residues was characterized.

Commercially available Nd–Fe–B sintered magnets were ground into fine powders (ca. 3 µm in diameter) by a planetary ball mill apparatus in air and then served as test specimens of powder scrap. The oxygen content was ca. 1 mass %. A mixture of 1.0 g of NH_4Cl (3 times excess for chemical equivalent) and 1.0 g of the powder scrap was charged in a Pyrex reactor tube (i.d. 10 mm) and heated at 523–623 K for 3–12 h in a N_2 gas flow. After the reactions, the resultant powders were soaked in distilled water. The soaked substance and solid residue were analyzed by an energy dispersive X-ray spectroscopy (EDX). The recovery rate of rare earths was evaluated on the basis of the (Nd + Dy)/Fe metal ratio of solid residue before and after the chlorination and soaking processes. Here, Dy element is especially desirable to use or reuse effectively due to its scarcity. In fact, the Dy content in the present magnet scrap is ca. 1 atom %. The solid residue was identified by X-ray diffraction (XRD) measurements using Cu Kα radiation. The specific surface area of the raw powder scrap and residual powders (after rinsing) was measured by the conventional nitrogen adsorption method (BET). Magnetic properties were characterized by a vibrating sample magnetometer (VSM).

Figure 1 shows the XRD patterns of the powder scraps before and after the chlorination at 573 K for 3 h. The XRD pattern of unreacted sample was assigned as the tetragonal phase of $Nd_2Fe_{14}B$ (curve a), but no obvious diffraction peaks was detected from the chlorinated powder (curve b). At low temperature (ca. 500 K), RCl_3 (R: rare earths) was reported to form from R_2O_3 by reacting with NH_4Cl through intermediate complex $(NH_4)_mRCl_{m+3}$ ($m = 2$: La–Gd, $m = 3$: Tb–Lu).[9] After soaking the chlorinated samples in distilled water, the XRD pattern only derived from cubic α-Fe phase was observed as shown in Figure 1 (curve c). These results suggest that the surface of powder scrap was covered with amorphous or low crystallinity RCl_3.

From the EDX data for this solid residue after soaking, one can evaluate that the rare earth content (Nd + Dy) is 1.2 atom %. The rare earth recovery rate was calculated to be ca. 87% as listed in Table 1. The metal ratio of Nd:Dy for the solid residue was nearly the same as the raw powder scrap, suggesting that the Nd and Dy possess a similar affinity against chlorine. Although a small amount of iron existence (ca. 7 atom %) was detected on the EDX analysis for the evaporated residue in the soaking solution, this amount is considerably small compared to the total iron content in the powder scrap. So it is concluded from above results that rare earth elements were almost selectively chlorinated under the applied reaction conditions. The rare earth recovery rate did not change (ca. 86%) even by elongating the reaction time (12 h). The reaction time of 3 h was enough to accomplish

Table 1. Rare earth [Ln: (Nd + Dy)] recovery rate from the $Nd_2Fe_{14}B$-based magnet powder scrap

Chlorination conditions	Elemental ratio/atom % Ln:Fe	Rare earth recovery rate/%
As-milled[a] (O_2: 1 mass %)	9.5:90.5	—
573 K, 3 h	1.2:98.8	87
573 K, 12 h	1.3:98.7	86
623 K, 3 h	3.2:96.8	66
623 K, 3 h[b]	1.0:99.0	90
523 K, 3 h	2.6:97.4	73

[a]Milling the $Nd_2Fe_{14}B$-based magnet by a planetary ball mill apparatus. [b]Twice amount of NH_4Cl was used.

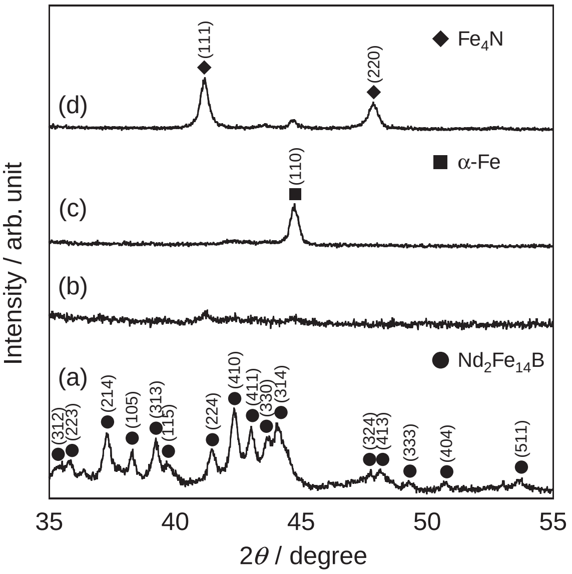

Figure 1. XRD patterns of the $Nd_2Fe_{14}B$ powder scrap: (a) raw powder, (b) as-reacted with NH_4Cl at 573 K for 3 h, (c) after rinsing (b) with distilled water, and (d) after the chlorination at 623 K for 3 h.

the almost overall chlorination for the powder scrap. Moreover, the chlorination increases the surface area of powder scrap from 2.3 to 23.5 m^2/g. This is one of the pieces of evidence in support of the selective chlorination for rare earths.

The recovery rate declined to ca. 66% with increasing the temperature to 623 K. This may be due to the evaporation of NH_4Cl at such high temperature and, by charging the twice amount of NH_4Cl to the standard one, the rare earth recovery rate increased to ca. 90%. It is also noted that α-Fe changed to Fe_4N owing to the nitridation with NH_3 liberated form NH_4Cl (Figure 1 curve d). On the other hand, the recovery rate was decreased to ca. 73% by lowering the reaction temperature to 523 K. Here, the unreacted NH_4Cl was detected after the reaction because the applied temperature was too low to decompose NH_4Cl completely.

In order to elucidate the chlorination mechanism on the powder scrap, the individual reactivity of rare earth and transition-metal elements was compared at 573 K for 3 h from each other. The chlorination thoroughly proceeded on the Nd metal or Nd_2O_3 powder to form $NdCl_3$. Also, α-Fe metal powder was chlorinated and generated $FeCl_2$ but the conversion was only about 30%, although the chlorination conversion of Fe_2O_3 powder reached to about 90%. This indicates that the reactivity of Fe_2O_3 with NH_4Cl is higher than that of α-Fe. For physically mixed Nd_2O_3 and α-Fe powders, high rare earth recovery rate was obtained (ca. 100%). The high recovery rate observed on the powder scrap should be responsible for the standard formation enthalpy difference between $NdCl_3$ and $FeCl_2$, where $FeCl_2$ generates during the chlorination and still reacts with Nd metal in the powder scrap to change Fe metal and $NdCl_3$. This also results in some additional improvement of the chlorination selectivity for rare earths.[8]

The resultant α-Fe powder derived from the powder scrap gave saturation magnetization values around $M_s = 1.4\,T$ with coercivity of $H_{cj} = 400\,Oe$. This magnetization value was somewhat low compared to the conventional value of pure α-Fe metal (2.15 T).[10] SEM observations for this powder reveal that the α-Fe powder is composed of very fine particles with the diameter less than 50 nm. The low magnetization value is due to the partial oxidation during the soaking treatment. On the contrary, the coercivity value of the present α-Fe powder is significantly larger than that of pure α-Fe metal (ca. 1 Oe).[10] The small size of primary particles is also responsible for the increase of coercivity. The spin alignment near the particle surface is random, so that the magnetic anisotropy of nanoparticles is larger than that bulky samples.[11] The Fe-based solid residue powders are expected to use as electromagnetic wave absorbers at higher frequency range due to the high magnetic anisotropy.[12] Further characterizations for them are in progress.

In conclusion, the rare earth elements in the Nd–Fe–B sintered magnet scraps with low oxygen content are successfully recovered in ca. 90% yield by using NH_4Cl as a chlorination reagent. This selective chlorination is due to the difference of standard formation enthalpy between RCl_3 and $FeCl_2$, so that RCl_3 is easily recovered by soaking the reacted solids. The Fe-based solid residue powder obtained as a by-product shows high coercivity around 400 Oe.

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