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Recycling of rare earth magnet scraps: Carbon and oxygen removal from Nd magnet scraps

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Abstract

The decarburization and deoxidation technique for permanent Nd–Fe–B magnet scrap is investigated. The carbon and oxygen contamination damage the magnetic properties. The carbon content decreased less than 0.001% by heating in air. The two stage deoxidation is applied, iron oxides are reduced by heating in hydrogen thereafter rare earth oxides are removed by Ca-reduction and leaching. The appropriate conditions for deoxidation in the Ca-reduction and suppressing the re-oxidation in the leaching are investigated. The heating pattern in Ca-reduction and the leaching condition for the mixture composed of Ca compounds and Nd–Fe–B alloy powder greatly affects the oxygen content of recycled material. The decarburized and deoxidized Nd–Fe–B magnet scrap can be recycled as alloying elements by melting.

Keywords: Permanent magnets; Recycle; Decarburization; Deoxidation; Induction melting

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1. Introduction

The waste of permanent Nd–Fe–B magnet increases year by year and its recycling becomes inevitable for reduction of industrial wastes, natural resources saving [1–3]. For example, boron that may be contained in acid dissolving sludge can pollute the underground water [4].

We previously reported a recycling process where scraps are returned to the conventional induction melting, as shown in Fig. 1 [5–7]. The treatments prior to melting consisted of two main subsequent steps. The first step is the carbon removal process as CO_2 gas by oxidation at high temperature in air. The second is the oxygen removal process by a combination of hydrogen-reduction and reduction-and-diffusion (RD) method using Ca and $CaCl_2$. In our previous work, the carbon and oxygen content could reach a level of 0.01% and 0.70%, respectively [5–7]; however, further removal of oxygen is required to promote practical application.

In the case that 30 mass% scraps are mixed with the virgin materials, the oxygen content of scraps should be kept less than 0.1% for proper processing, namely high quality and high yield production and slight crucible damage through the effect of decreasing RE oxides slags.

In the following the subsection, we discuss the oxygen decreasing for induction melting and the effect of RD conditions (heat treatment temperature, particle size and Ca removal) on oxygen removal for the decarburized Nd–Fe–B magnet.

2. Experimental procedure

The material used in this study was a grinding sludge generated in the machining process of Nd–Fe–B magnet. Firstly, the foreign bodies like plastic splinters (about 10 mm in width) were sifted through a screen. The slurry was squeezed by a conventional filter press, and clay-like compacts were obtained.

Secondly, these compacts were heated at 1073 K for 3.6k s in air for decarburization. The free carbon and the RE carbides

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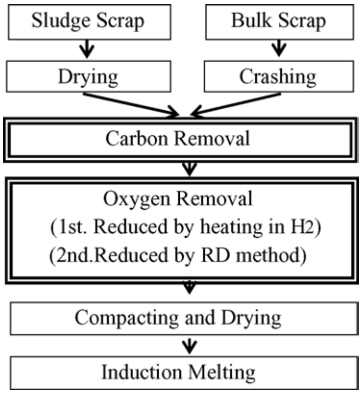

Fig. 1. Schematics of the recycling process for Nd–Fe–B magnet.

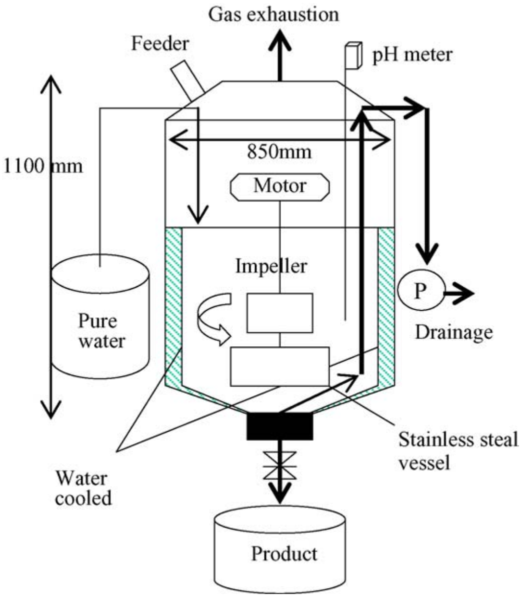

Fig. 2. Vertical sectional view of the "bench-scale" experimental arrangement.

in the scraps converted to CO_2 gas by oxidizing effect of O_2 in air at elevated temperature [5]. The decarburized but oxidized scrap was milled, and classified below 0.5 mm in N_2 gas atmosphere, then heated in H_2 atmosphere at 1253 K for 28.8k s to eliminate the undesirable iron oxide [5,6]. The powder treated by hydrogen-reduction in the remaining RE oxides was re-milled and served for subsequent RD process.

The conditions of Ca-reduction will be described briefly, since the details were reported elsewhere [5–7]. The hydrogen reduced scrap powder was mixed with 10 mass% powdery anhydrous $CaCl_2$ (95 mass% purity) in N_2 gas atmosphere. Ca shots (1–3 mm in diameter, 95 mass% purity) were added to the mixture. The amount of Ca was adjusted to be 1.35 times the stoichiometric necessity assuming that it is oxidized to CaO. About 3 kg of the mixture was charged into a stainless steel vessel and 10 vessels were heated at 1223 K in Ar atmosphere at 105 kPa for appointed duration, then heated at 923 K for alloying. The product after Ca-reduction was milled below 5.0 mm in N_2 gas atmosphere.

Residual Ca, by-product CaO and solvent $CaCl_2$ were leached with cooled pure water and the supernatant solution was decanted. The leaching experiments were carried out in two scales (beaker- and bench-scale). The beaker-scale was performed with a small stirrer (80 mm in width) and 2-l Pyrex beakers. The bench-scale experimental arrangement test is shown in Fig. 2. A 400-l vessel equipped with double stage paddle impellers was used. The impellers were designed for preferable flow characteristics to generate a uniform suspension of solid particle and to prevent fragile particle from breakage.

These leaching operations were repeated until the pH value of the solution becomes less than 10.5. The leached powder was squeezed by mechanical press (50 mm in diameter), and dried in vacuum. In this paper, we concern about the leaching conditions; therefore, the words "beaker-scale" or "bench-scale" described in graphs are indicated for the sake of simplicity.

The chemical composition was measured with ICP-AES, and the amounts of carbon and oxygen were measured with LECO-TC-366 and LECO-CS-444, respectively. The mean particle size was measured by using the air permeability method (Fishier Sub Sieve Sizer). The observation of sample morphology, the surface composition and the phase identification were carried out by using an optical microscope, EDX and X-ray diffraction (XRD), respectively.

3. Result and discussion

3.1. Decarburization and hydrogen-reduction

The carbon content was decreased to a level of 0.001 mass% from the original 1.3 mass% in the tested sludge by heating in air, and the oxygen content decreased to a level of 8.5% mass from 23.0% by the subsequent hydrogen-reduction. Its chemical composition is shown in Table 1.

After the hydrogen-reduction, the sample was identified as a mixture of α-Fe, $FeNdO_3$ and $NdBO_3$ by XRD. Fig. 3 shows an optical microscope image of a cross-section for the obtained sample. Porous and fine structure, and the α-Fe mainly surrounded by $NdFeO_3$ and $NdBO_3$, are observed.

Table 1
Chemical composition of the decarburized sludge scraps

Elements	Mass%
Nd	18.2
Pr	5.3
Dy	4.6
B	0.9
Co	0.8
Fe	Bal.
O	8.5
C	0.001

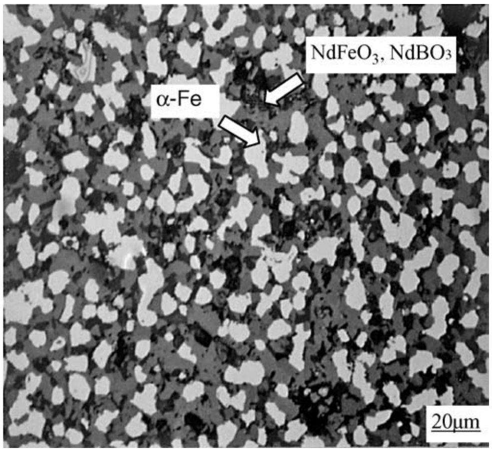

Fig. 3. Optical microscope image of cross-section of the decarburized powder.

3.2. Conditions for Ca-reduction

The decarburized powder, which phases consisted in $NdFeO_3$, $NdBO_3$ and α-Fe, was served to Ca-reduction and "bench-scale" leaching, then the reduced powder was obtained. Only the $Nd_2Fe_{14}B$ ferromagnetic phase and residual α-Fe phase were identified by XRD. Fig. 4 shows the effects of the heat treatment time on the amount of oxygen and α-Fe of the reduced powder, which was evaluated assuming that the intensity ratio of XRD is proportional to each volume ratio of the phases. The oxygen content decreased when the heat treatment was prolonged. The amount of α-Fe was experimentally correlated with the residual oxygen concentration. The RE content of sludge powders used in this study is slightly richer than that of the $Nd_2Fe_{14}B$ composition. An increase of the α-Fe phase of the reduced powder is balanced with the amount of RE-rich phases from the viewpoint of the composition balance. Therefore, as the amount of α-Fe phase of the reduced powder decreases, the amount of $Nd_2Fe_{14}B$ phase through the reduction-alloying reaction increases, instead. This reason will be discussed as follows.

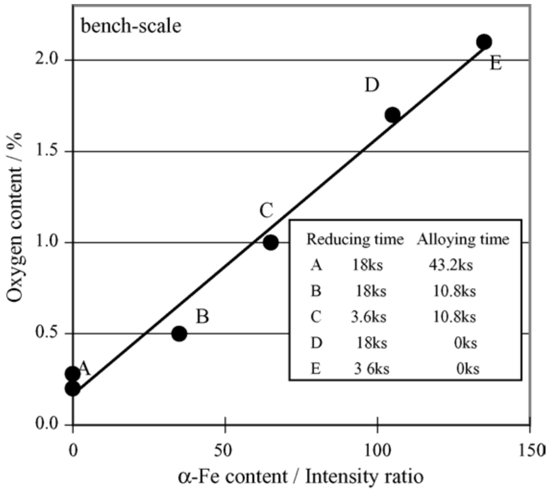

Fig. 4. Effects of the conditions of Ca-reduction on the amounts of both oxygen and α-Fe of the reduced powder.

The complex oxides, $NdFeO_3$ and $NdBO_3$, would be individually co-reduced to the metallic state by the reaction with Ca, and the additional alloying between [Nd–Fe] and [Nd–B] alloys would occur simultaneously as

$$NdFeO_3 + 3Ca = [Nd\text{–}Fe] + 3CaO \quad (1)$$

$$NdBO_3 + 3Ca = [Nd\text{–}B] + 3CaO \quad (2)$$

$$\alpha\text{-}Fe + [Nd\text{–}Fe] + [Nd\text{–}B] = Nd_2Fe_{14}B \quad (3)$$

In the case of short period alloying heat treatment, the RE-rich metallic phases such as [Fe–Nd] and α-Fe phase sometimes remained without forming $Nd_2Fe_{14}B$ phase by Eq. (3). These intermediate RE-rich metallic phases are easily oxidized during leaching because of their high reactivity with water [8,9]. Therefore, the disappearance of α-Fe phase relates closely with the residual oxygen content. Fig. 5 illustrates the formed phases and oxidation resistance during handling in the perfect and imperfect reactions.

3.3. Effects of the particle size of the initially decarburized powder

The decarburized powder was ball-milled in Ar atmosphere to prepare 0.045–0.1 mm sample and 0.1–1.0 mm sample by sieving. Heating pattern 'A' in Fig. 4 was applied for reduction. Fig. 6 shows the relationship between the particle size of the decarburized powder and the oxygen content of the reduced powder. The finer powder could attain lower oxygen content. This behavior can be understood by considering that the α-Fe shell surrounding the particles is thinner in finer powder and that the mass transfer in this shell is faster. And some portion of RE oxides is directly exposed to Ca liquid because of its large surface area. For practical application, pulverizing less than 0.1 mm of the decarburized powder is needed prior to reduction.

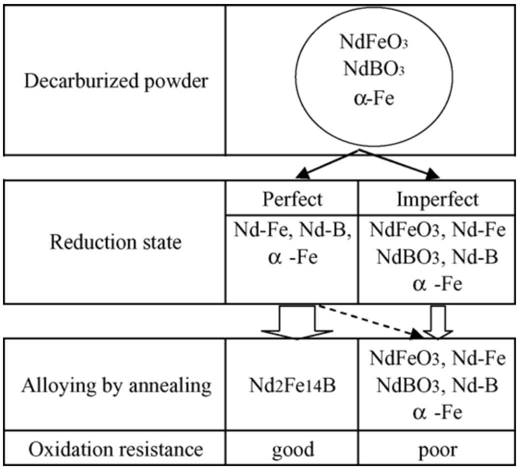

Fig. 5. Evaluated reducing mechanism of Nd–Fe–B magnet scraps by reduction.

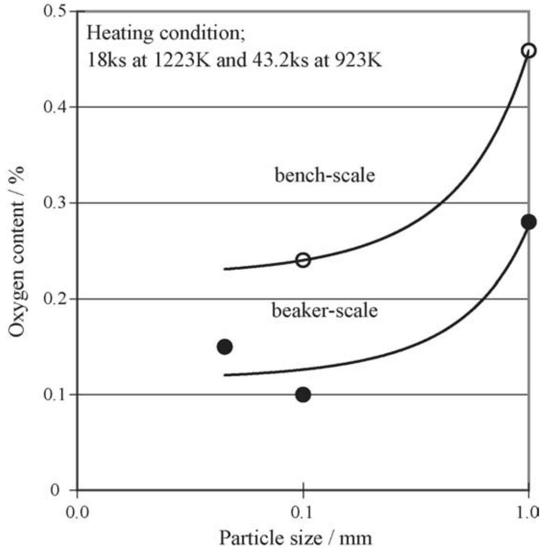

Fig. 6. Effects of the particle size of the decarburized powder on the oxygen content on the reduced powder.

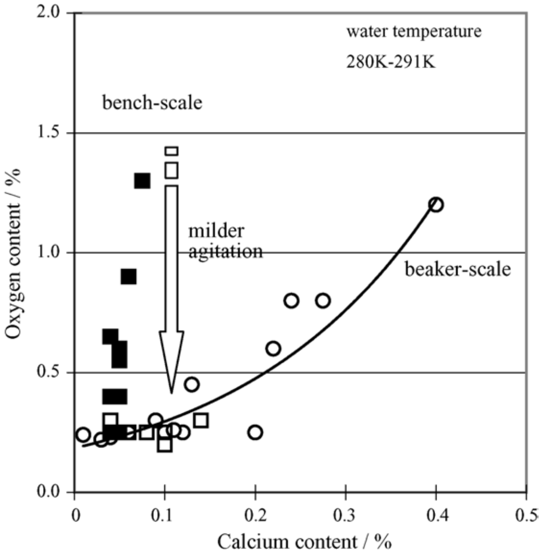

Fig. 8. Effects of the leaching conditions on the amounts of both calcium and oxygen of the reduced powder.

3.4. Addition of Fe_2O_3 for in situ coarsening

In contrast, the coarser powder is more resistant against surface re-oxidation during leaching. The in situ coarsening during Ca-reduction was conducted using the large exothermal reaction heat between Fe_2O_3 and Ca. The commercial Fe_2O_3 powder (about 1 μm) was uniformly added to the decarburized powder.

Fig. 7 shows the relationship between the oxygen content and the particle size of leached powder. The particle size was measured by Fischer Sub Sieve Sizer. The oxygen content decreased to 0.12 mass% and the powder became two times coarser when 8 mass% Fe_2O_3 powder added. When 12 mass% Fe_2O_3 was added, however, the oxygen content increased. In addition, the Ca content was increased by about three times compared to the case of 8 mass% addition. This is because the by-product CaO was captured inside the reduced powder due to the extremely large heat of the exothermic reaction. In fact, a part of the iron was melted during reduction.

3.5. Leaching conditions

Re-oxidation of the reduced powder in leaching was enhanced by its large specific surface area and a rise of powder surface temperature. The former is due to mechanical breakage by stirring, and the latter is due to an exothermic calcium hydration.

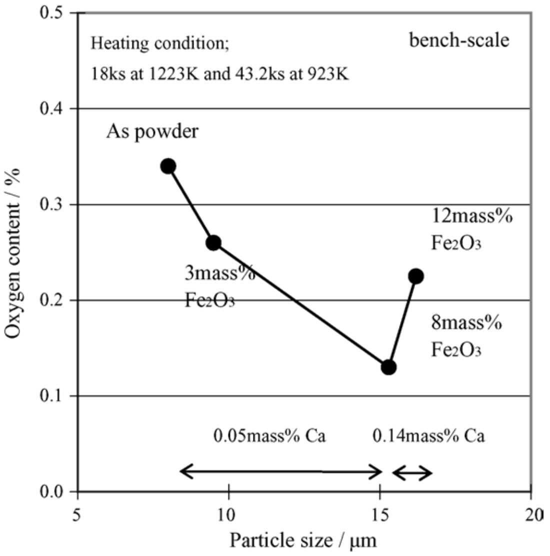

Fig. 7. Relationship between the particle size and the oxygen content by varying amount of Fe_2O_3.

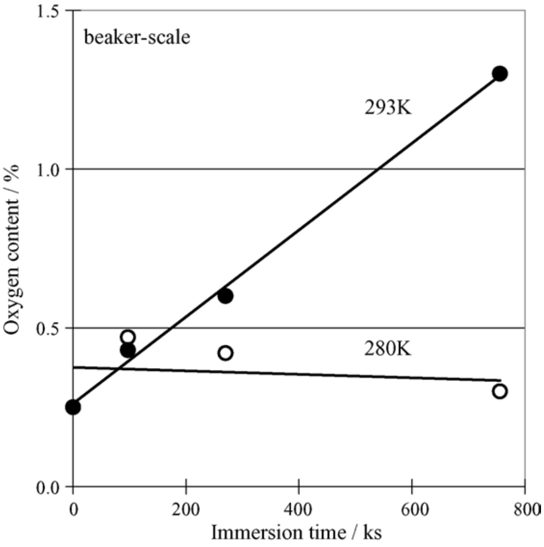

Fig. 9. Effects of the water temperature on oxygen content of the reduced powder.

Fig. 8 shows the relationship between O content and Ca content among the various leaching conditions. The decrease of Ca content leads to the decrease of oxygen especially in the beaker-scale tests. This means that an efficient removal of by-product CaO from the powder contributes greatly to decrease the oxygen content. In a bench-scale test, the agitating condition was studied. The milder agitation or the intermittent agitation prevented re-oxidation.

Fig. 9 shows the influence of the water temperature on the oxygen content of the leached powder. The reduced powder was leached in advance using the bench-scale apparatus, and subsequently immersed in pure water. Immersed in 293 K, the oxygen content increased with time, while the re-oxidation could be suppressed in 280 K water.

4. Conclusions

In order to remove carbon and oxygen in the Nd–Fe–B sludge scraps, the sludge was once decarburized by oxidation, and then heated in H_2 gas to reduce Fe_2O_3 followed by Ca-reduction to reduce RE oxides. The optimum conditions for Ca-reduction and leaching were studied to lower the oxygen content. A longer reaction time eliminated α-Fe in Ca-reduction and finer initial powder were preferable. The carbon content of decarburized and reduced material was less than 0.001%. A level of 0.1 mass% O was achieved in beaker-scale test. In situ coarsening of the powder by Fe_2O_3 addition was effective to suppress the surface re-oxidation during leaching. A mild agitation and lower temperature during leaching was also preferable.

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