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Recycling of Rare Earth Magnet Scraps Part III Carbon Removal from Nd Magnet Grinding Sludge under Vacuum Heating

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The removal of the carbon from Nd magnet scraps is indispensable for high-quality recycling by the induction melting method as a preliminary process. The Nd magnet scraps can be decarburized to a level of less than 0.03 mass% by using an oxygen source at high temperatures, as reported in Part 1. The decarburized Nd magnet scraps can then be deoxidized by using the Ca reduction to a level that allows commercial melting in an induction furnace, as reported in Part II. However, the undesirable iron oxide (Fe_2O_3) which causes a disadvantage for Ca reduction is inevitably generated by using an oxygen source at high temperatures. The aim of this work is to investigate an economical decarburization method in which only the carbon sources in Nd magnet scraps are decarburized, without generating iron oxide. The grinding sludge as Nd magnet scraps is effectively decarburized to a level of less than 0.03 mass% without generating any iron oxide by heating at above 1073 K under a pressure of less than 5.32×10^{-2} Pa. The amount of oxygen in the decarburized powder is about 8 mass%, which is lower in comparison with its value in Part 1. In this report, the decarburization mechanism under reduced pressure using the grinding sludge, and its economic significance prior to the decarburizing method described in Part 1, are discussed.

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1. Introduction

The amount of production of the permanent Nd–Fe–B magnet as a very important electronic part incorporated in current electronic devices has been expanding. However, about 50% of the total amount of production becomes waste in the form of bulky scrap and powdery scraps, because the permanent Nd–Fe–B magnets are produced by powder metallurgy processes which consist of, for example, the mechanical pulverizing of material ingots, the compaction in the magnetic field, the sintering of green compact, and machining (mainly grinding).[1–3] As for the high content of expensive rare earth metal (Nd, Pr, Dy) in these scraps, about 30 mass%, some effective recycling process needs to be developed. However, the present recycling ratio is only slightly less than 10% and the majority of the scrap is discarded as industrial waste.[4]

For the above problem, we have shown that an economical method of returning the scraps to the conventional induction melting is possible by preliminary removal of both carbon and oxygen prior to melting by using the combined techniques of high temperature oxidation, reduction in hydrogen atmosphere, and Ca reduction, as reported in Part I and Part II.[4,5] As described in Part I,[4] the bulky scrap and the powdery scrap are completely oxidized in the air at above 1237 K, but even the ferromagnetic $Nd_2Fe_{14}B$ matrix phase in which carbon is free, is oxidized and iron oxide (Fe_2O_3) is generated. This iron oxide influences unfavorably the subsequently Ca reduction for two reasons, as follows: firstly, more Ca, which is required for the reduction of Fe_2O_3, increases the recycling costs; secondly, the reduction of Fe_2O_3 by using Ca generates a heat of reaction, as the fused iron can be formed like the reactive type shown in the following formula:[6]

$$Fe_2O_3 + 3Ca(\lambda) = 3Fe + 3CaO: \Delta H^0_{1273\,K} = -1117\ \text{kJ/mol}$$

This exothermic reaction causes not only the partial melting of the reduction vessels but also yields the low recovery of reduced scraps because of the strong deposition between them. This iron oxide can be reduced to α-Fe by heating in a hydrogen atmosphere, as described in Part I,[4] but this process causing more costs for the decarburizing process before Ca reduction is expected to be excluded.

Therefore, as an improved method for the high temperature oxidation in air described in Part I,[4] we have studied a new decarburizing process under reduced pressure to decarburize the scraps using the least amount of oxygen without generating unfavorable iron oxide. Consequently, regarding the grinding sludge, the amount of carbon decreases to the level of the high temperature oxidation technique (< 0.03 mass%), and the amount of oxygen gave a better result (about 8 mass%). On the other hand, the bulky scraps were not decarburized.

Concerning the decarburized grinding sludge, it was confirmed that a good quality reduced powder, which has a low amount of carbon (< 0.03 mass%) and oxygen (< 0.7 mass%), can be produced.

In this report, the decarburizing condition (heat temperature, heat time) and the decarburizing mechanism of the grinding sludge under reduced pressure are investigated, and the possibility for a low cost decarburizing process (lower amount of oxygen in scraps after decarburization) for the bulky scraps, *etc.* is presented.

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2. Experimental Procedure

In the first step, the effects of the heat treatment temperature on the amount of carbon and oxygen, and the morphology of the grinding sludge, were investigated under constant heat treatment time and reduced pressure. The tested scrap was the grinding sludge generated in the machining process of the Nd magnet. The water content in the sludge was 40 mass%. Initially the grinding sludge was dried in a vacuum for 36 ks at 333 K. Next, the foreign bodies of about 10 mm in width (Many are plastic splinters) were classified by using a metallic sieve with 1 mm opening, and the powder below 1 mm was subjected to decarburization.

The heat treatment was carried out using a furnace, of which the atmosphere can be adjusted, and by varying temperature. 150 g of powder was enclosed in a stainless steel vessel and was heated for 10.8 ks at 5.32×10^{-2} Pa, then cooled down in an Ar atmosphere. The heat treatment temperature was varied from 873 to 1473 K.

In the second step, the effects of the heat treatment time on the amount of carbon and oxygen, and the morphology of the grinding sludge, were investigated under constant heat treatment temperature and reduced pressure. The tested scrap was the same that described above. The heat treatment was carried out by varying the time. 150 g of powder was enclosed in a stainless steel vessel and was heated at 1343 K at 5.32×10^{-2} Pa, then cooled down in an Ar atmosphere. The heat treatment time was varied from 10.8 to 72.0 ks.

In the third step, the deoxidizing characteristics of the decarburized powder under reduced pressure were investigated using the Ca reduction method.[4,7–9] The tested samples was the powder decarburized at 1343 K for 10.8 ks under reduced pressure. Anhydrous $CaCl_2$ of 95 mass% purity was used for flux, and Ca shots of 7 mm in diameter and 95 mass% purity were used for the deoxidizing agent. 50 g of Ca were added to the sample. This amount was three times the reactive equivalent, which deoxidized as CaO. The amount of flux was 5 mass% of the sample, and sufficiently mixed in an Ar atmosphere. After the mixed sample was enclosed in the vessel, it was then heated in an Ar atmosphere at 1173 K for 7.2 ks, and finally cooled to 298 K. The Ca reduction product disintegrated completely in pure water below 288 K and slurry, containing reduced magnet powder, was obtained. The remaining Ca, the by-product CaO, and the solvent $CaCl_2$ were, then removed by leaching. After the solution had been disposed of, the reduced powder was dried in a vacuum at 288 K.

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 calculated as a weighted mean diameter (dp50) by using the weight multiplication curve, which had been obtained by sieving 50 g of the sample.

As for the morphology of the decarburized powder, the cross-sectional structure was investigated with a scanning electron microscopy. The surface analysis and the phase identification were carried out by EDX and X-ray diffraction. As for the morphology of the reduced powder, the surface was investigated with a scanning electron microscopy and the phase identification was carried out by X-ray diffraction.

Table 1 Chemical composition of the dry grinding sludge.

Elements	Nd	Pr	Dy	B	Co	Fe	O	C
mass%	19.5	6.0	4.2	0.8	0.8	bal	5.6	1.3

3. Results and Discussions

3.1 Characterization of the grinding sludge scraps

The characterization of the grinding sludge scraps is briefly described as follows. The grinding sludge is the form of slurry which is generated in the machining process of the Nd–Fe–B sintered body, and the mean particle size is about 1 μm.[4] The phases of the grinding sludge are mainly the $Nd_2Fe_{14}B$ matrix phase and the RE rich phase, as described in Part I.[4]

The composition of the dried grinding sludge is shown in Table 1.

Regarding the forms of carbon in the dried grinding sludge, they are (1) the carbides in the RE rich boundary phase (the amount of the carbon is 0.05–0.08 mass%), (2) the water-soluble grinding oil (the amount of the carbon is 0.1–0.15 mass%), (3) the carbon powders issuing from the carbon plate when cut together with the magnets.[4] In this report, both the grinding oil and the carbon powders are defined as the free carbon. With regard to oxygen in the dried grinding sludge, it is considered that it exists in some adherent water,[10] which comes from the water-soluble grinding oil and in the oxygen rich RE phase. Assuming the oxygen rich RE phase is fully oxidized as Nd_2O_3, the amount of oxygen is about 4.5 mass%. The difference between the amount of oxygen as fully oxidized Nd_2O_3 and that of the tested sample shown in Table 1 is considered as the adherent water.

3.2 Effects of the heat treatment temperature on the decarburization under reduced pressure

Figures 1(a) and (b) show the variation of the amount of carbon and oxygen of the heated sample with various conditions of heat treatment temperature under constant heat treatment time and furnace pressure. The amount of carbon was decreased drastically at above 873 K, and reached 0.03 mass% at 1073 K. This decrease is considered to be due to the removal of the free carbon, as previously described. The reason why this decarburization occurred under reduced pressure is presumed to be because some adherent water of the dried grinding sludge decarburized the free carbon as CO gas, according to the reaction mechanism described below.[6]

$$H_2O + C = CO(g) + H_2(g) : \Delta G0 < 0 \text{ at above } 773\,K$$

At more than 1073 K the amount of carbon slowly decreased from about 0.06 mass% to 0.02 mass%. The mechanism of this slow decrease is assumed to be as described below.

Figure 1(c) shows the variation of the mean particle size of the heated sample under various conditions of heat treatment temperature. They were drastically coarsened at above 1073 K, and reached about 400 μm in diameter.

Figures 2(a) and (b) show a SEM image of the dried grinding sludge and the EDX image of the decarburized powder heated at 1437 K. It reveals a porous structure and the sam-

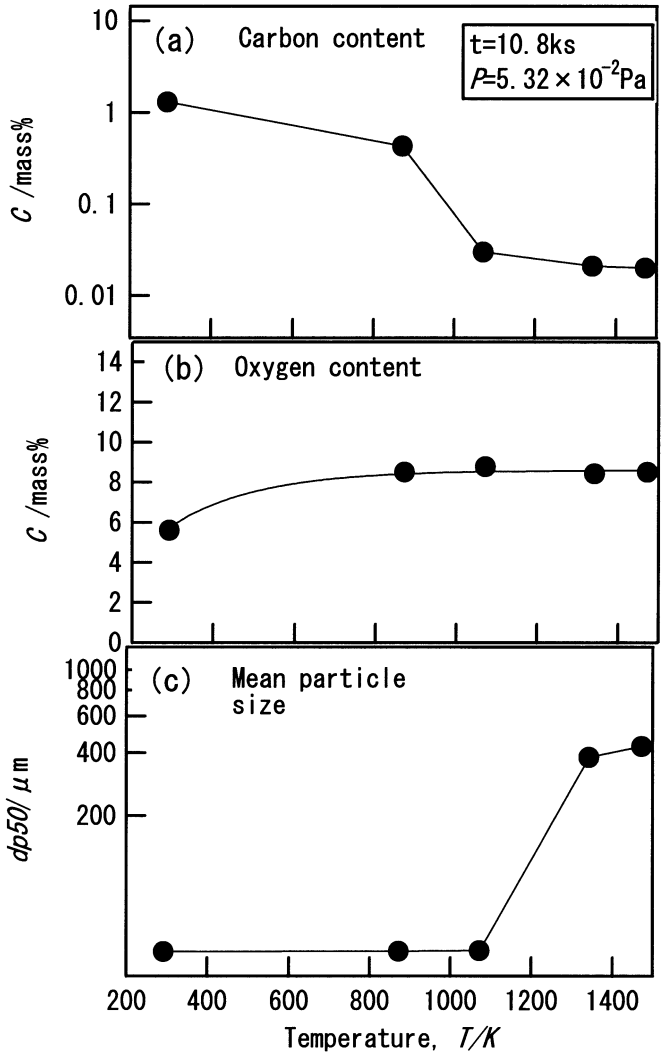


Fig. 1 Relationship between the heat treatment temperature and (a) carbon concentration, (b) oxygen concentration, (c) mean particle size of the decarburized powder.

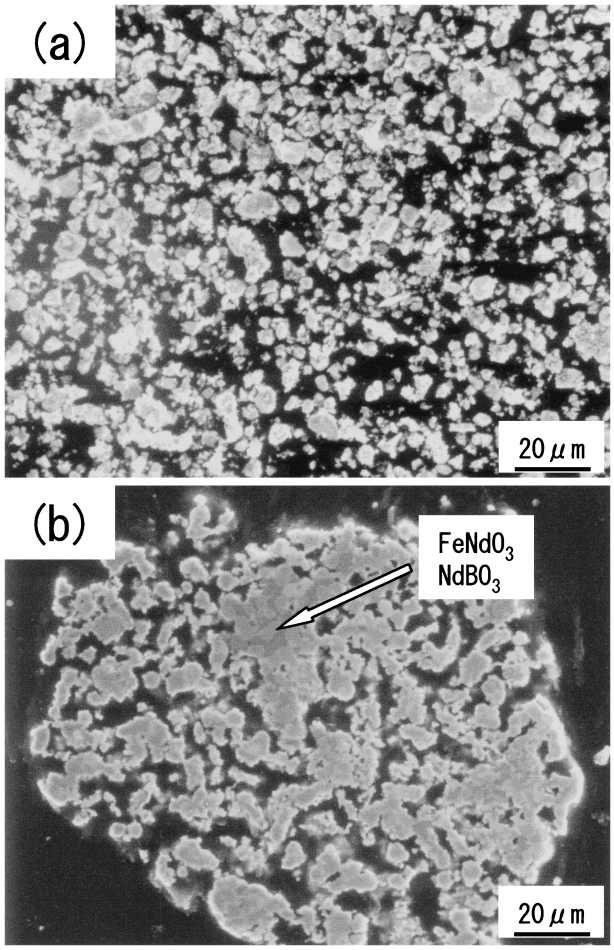


Fig. 2 SEM image of (a) dry grinding sludge and EDX image of (b) cross section of the decarburized powder.

ple powders are lightly sintered from each other and formed neck parts in which RE and oxygen concentrated. The phases of the decarburized powder consist of α-Fe, $FeNdO_3$, and $NdBO_3$ by X-ray diffraction. Consequently, the neck parts consisted of RE rich phases, which are presented as $FeNdO_3$ and $NdBO_3$.

That is to say, regarding the grinding sludge, the powders are lightly sintered at above 1073 K, and the RE rich phase is concentrated in the neck parts.

It is a well-known phenomenon that the liquid sintering of the Nd–Fe–B permanent magnet becomes noticeable at above 1100 K.[11,12] Moreover, it is revealed that the RE rich phase at the neck parts makes it easy for them to contact with oxygen in the atmosphere according to its porous structure. From the above facts, it is considered that the decrease of the amount of carbon at above 1073 K results in the decarburizing of RE rich phase by diffusing small amounts of oxygen which come from some adherent water or the atmosphere into the RE rich phase.

The amount of oxygen slowly increased as the heat treatment temperature rose. There was a slight increase at 1423 K, but this value is extremely low compared with the high temperature oxidation method, as described in Part I.[4] As for this oxygen increase, it is assumed that oxidation of the RE rich phase is inevitable even under 5.32×10^{-2} Pa according to the Nd–Nd_2O_3 oxygen potential diagram.[13]

3.3 Effects of the heat treatment time on the decarburization under reduced pressure

The influence of the heat treatment time on the decarburization was investigated at temperature (1343 K), which is presumed to be that the decarburization efficiently proceeds under reduced pressure as described above.

Figures 3(a) and (b) show the variation of the amount of the carbon and oxygen of the heated sample with various conditions of heat treatment time under constant heat treatment temperature and furnace pressure. When the amount of carbon was decreased to a level of 0.02 mass%, more than 10.8 ks of time was revealed to be required for sufficient decarburization. The free carbon is presumed to be decarburized for a short time, according to the amount of carbon decrease.

The amount of oxygen became saturated for more than 10.8 ks; there was a slight increase. This amount of oxygen increase is supposed to be a result of the reaction with a small amount of oxygen in the atmosphere, as described in **3.2**. The dried grinding sludge turns out coarser according to the liquid sintering of the RE rich phase that has strong affinity with oxygen as shown in Fig. 3(c).[11,12] This is because there is a

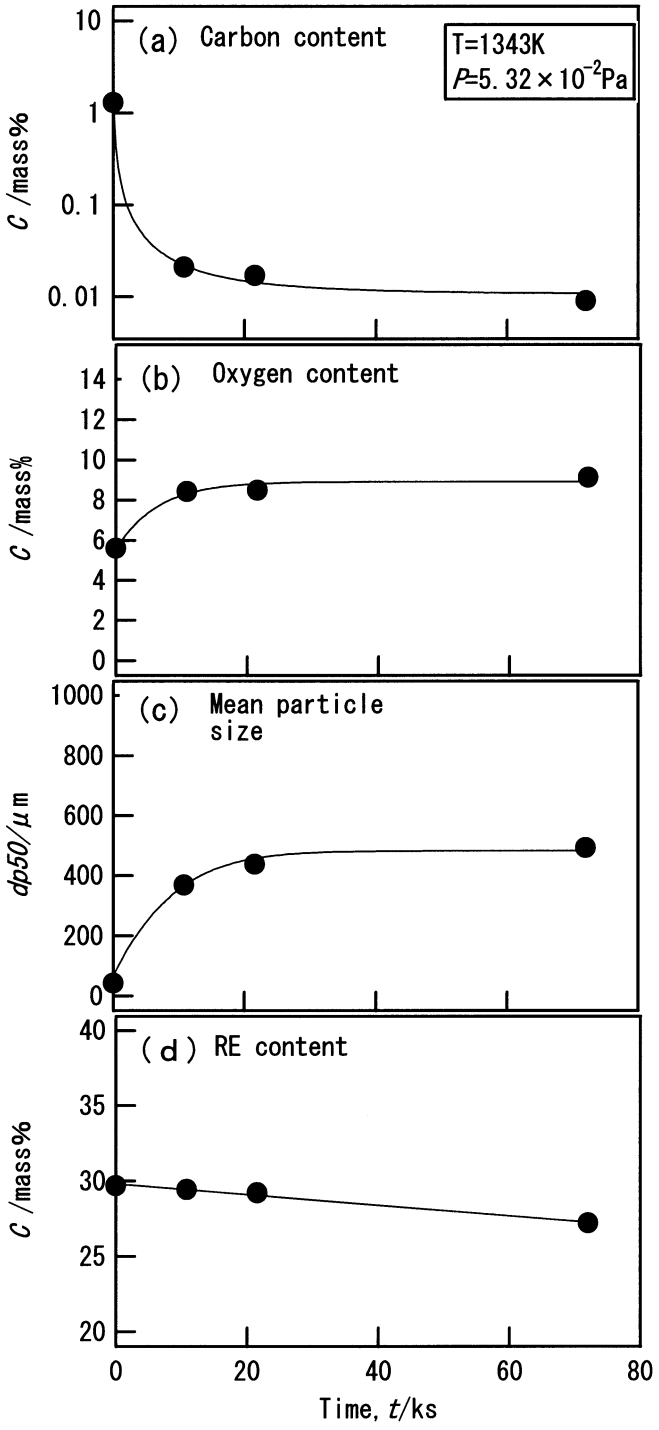


Fig. 3 Relationship between the heat treatment time and (a) carbon content, (b) oxygen content, (c) mean particle size, (d) rare earths concentration of the decarburized powder.

strong relationship between the increase in the oxygen resulting from the heat treatment time and the increase of the mean particle size of the heated powder.

Figure 3(d) shows the variation of the amount of RE. About 2 mass% of RE is decreased under heat treatment for 72 ks, but this is assumed to be due to a material balance with the oxygen increase, and the heat treatment under reduced pressure has little influence on the loss of the rare earth.

To summarize the above: concerning the decarburizing of the dried grinding sludge, the free carbon and the carbides at the grain boundary are efficiently decarburized by some adherent water and a small amount of oxygen in the atmosphere to a level of 0.03 mass% without generating undesirable iron oxide, even under reduced pressure.

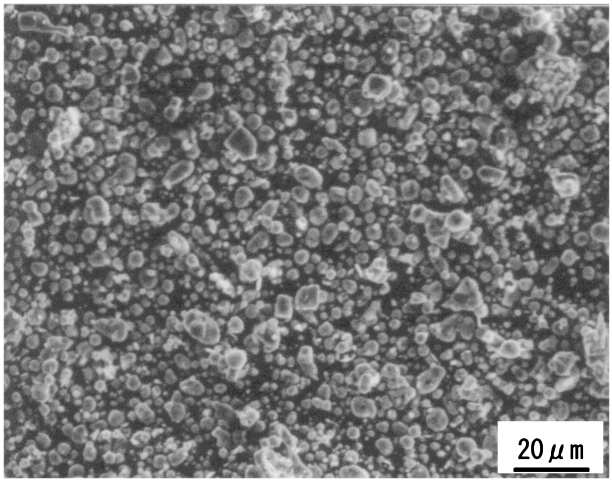


Fig. 4 SEM image of the decarburized powder reduced by the Ca–Ca halide flux deoxidation method.

In our current investigation, the scatter of the amount of carbon and oxygen of the grinding sludge ranges from 1.0 mass% of carbon and 5.0 mass% of oxygen to 1.5 mass% of carbon and 10.0 mass% of oxygen. We confirmed that the scatter of the amount of carbon of heated powder under reduced pressure ranges from −0.01 mass% to +0.01 mass%, and this decarburizing method is reproducible.

3.4 Effects of the Ca reduction on the decarburized powder under reduced pressure

The application of the Ca reduction method described in Part II[5] to the decarburized grinding sludge under reduced pressure was investigated.

The tested samples was the decarburized powder heated for 10.8 ks at 1343 K under reduced pressure.

Figure 4 shows the SEM image of the decarburized powder that was deoxidized by the Ca reduction. Their morphology shows spherical powder in comparison with the dried grinding sludge shown in Fig. 2(a).

The reason for this was presumed to be that the oxygen rich phase ($FeNdO_3$, $NdBO_3$) concentrated in the neck parts had been deoxidized by Ca, and dropped out as the reduced RE rich powder in the subsequent leaching process.

The variations of carbon, oxygen, rare earth, and calcium concentrations of the decarburized powder before and after deoxidation are shown in Table 2. It was confirmed that the amount of oxygen can decrease to the same level of 0.7 mass% as sintered magnet scraps. The amount of Ca also decrease to a level of 0.08 mass%, which leads to an industrial application for the induction melting. On the other hand, the recovery of the reduced powder to the tested sample was 51 mass%. This might be mainly due to the effusion of reduced powder while leaching, an improved leaching process in which the reduced powder can not flow out is expected in the future. As the peak of the $Nd_2Fe_{14}B$ matrix phase is identified by the X-ray diffraction, it is presumed that the reduced alloy powder, which has almost the same properties as the

Table 2 The variations of carbon, oxygen, rare earth, and calcium concentrations of the decarburized powder before and after the deoxidation treatment

(mass%)

Before deoxidation				After deoxidation				Yield
C	O	R	Ca	C	O	R	Ca	
0.02	7.83	29.5	<0.01	0.02	0.67	29.2	0.08	51

Nd–Fe–B alloy can be obtained.

4. Conclusions

The effects of the heat treatment conditions on decarburization under reduced pressure and a decarburizing mechanism for the grinding sludge of the Nd–Fe–B permanent magnet were studied. The application of the Ca reduction to the decarburized powder was also investigated, and the following findings were obtained.

(1) The amount of carbon in the grinding sludge scraps of the Nd–Fe–B permanent magnet can be reduced from 1.3 mass% to a level of less than 0.03 mass% by decarburization under reduced pressure (5.32×10^{-2} Pa) for 10.8 ks at 1073 K. Generation of undesirable iron oxide (Fe_2O_3) did not occur.

(2) Regarding the decarburizing mechanism of the grinding sludge under reduced pressure, the free carbon and the carbides in the neck part of the coarsened powder are presumed to be decarburized mainly by some characteristic adherent water as oxygen sources.

(3) The amount of oxygen in the decarburized powder under reduced pressure can be decreased to a level of 0.7 mass% by the Ca reduction method.

(4) Regarding an economical decarburizing method for bulky scraps, it is expected that only the carbides in the grain boundary can be decarburized by some sources of oxygen after a preliminary fine-ground pulverizing.

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