

## Recycling of Rare Earth Magnet Scraps: Part II Oxygen Removal by Calcium

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Powder scraps of neodymium-iron-boron permanent magnet were deoxidized by using calcium vapor, liquid or  $\text{CaCl}_2$  melt at 1223–1273 K. Because the scraps react with the acidic solutions during leaching of the byproduct  $\text{CaO}$ , the methods for removal of the excess amount of Ca and  $\text{CaO}$  were studied. When pH was controlled at about 8 during several times leaching, the dissolution of rare earth elements could be minimized. Ca vapor deoxidation could not supply enough amount of Ca through  $\text{CaO}$  layer. When a large amount of  $\text{CaCl}_2$  was added, the dissolution rate of  $\text{CaO}$  into the aqueous solution became faster, but some amounts of rare earth components were lost. The deoxidation by Ca liquid and 5 mass%  $\text{CaCl}_2$  and the subsequent leaching in distilled water with  $\text{pH} > 8$  gave the better result so that oxygen, even in heavily oxidized scraps, could be lowered to 0.7 mass%.

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### 1. Introduction

Oxygen in permanent Nd–Fe–B magnet scraps causes many technical problems on melting for recycling. For example, it is difficult to re-melt the oxidized magnet perfectly, partially because the melting temperature of  $\text{Nd}_2\text{O}_3$  is 2593 K.<sup>1</sup> The oxide flux prevents a sound casting due to its high viscosity, reacts with the alumina crucible or lying, and shortens the crucible lifetime.

However, oxygen contamination in the rare earth magnets is unavoidable. The  $\text{Nd}_2\text{Fe}_{14}\text{B}$  magnet phase is surrounded by the oxygen-rich phases at the grain boundary in order to achieve a strong cohesive force. The total amount of oxygen in the commercial magnets is a level of only about 0.3 mass%. The resin for bonding the magnetic powders is one of the main oxygen sources in so-called “bond magnet”. The organic layer protecting from the oxidation and corrosion is another source. It is difficult to remove mechanically these organic substances containing oxygen. Once the coating is removed for recycling, the magnet surface begins to oxidize significantly even in air. These oxide adhered to the surface becomes the new oxygen source in scrap handlings. As the other scrap source, a fairly large amount of magnet scrap is currently formed in the magnet producing processes. Especially the fine powder scraps in the conventional powder metallurgy or at the machining operation are heavily oxidized. The deoxidation prior to the melting is needed for perfect recycling.

This work will report the method to remove oxygen from the Nd magnet scraps. The procedure of oxygen removal is placed before melting in the total concept for our scrap recycling process, as reported in Part I.<sup>2</sup>

The inhomogeneity in chemical composition will be resolved in the melting. If the scrap is contaminated by carbon, carbon is removed prior to the oxygen removal process reporting here. Therefore, the oxygen removal process studied here will accept the normal scraps as well as the decarbonized scraps reported in Part I and III.<sup>2,3</sup>

Calcium was chosen as the reductant. It has a strong thermodynamic affinity with oxygen, and it is thermodynamically possible that Ca reduces  $\text{Nd}_2\text{O}_3$  directly to metallic state.<sup>1,4</sup> We expected that Ca can reduce even the oxidized scraps in which many oxide phases coexisted after carbon removal.<sup>2,3</sup> For example, the reduction-diffusion (RD) method using Ca from the mixture of  $\text{Nd}_2\text{O}_3$ , Fe and FeB was developed to form directly  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  magnet alloy, resulting that 0.27 mass%O remained in the magnet.<sup>5,6</sup> Because the oxygen solubility in pure Nd was 0.1–0.18 mass%O,<sup>7</sup> there is still some space to remove oxygen.

The Ca deoxidation was therefore applied in the metals reactive with oxygen, such as titanium,<sup>8–12</sup> zirconium,<sup>12–14</sup> niobium,<sup>12,15,16</sup> yttrium,<sup>17</sup> and rare earth metals.<sup>18,19</sup> Kamihira *et al.*<sup>19</sup> reported that 250 mass ppm oxygen in pure Nd was achieved by using the Ca–CaO equilibrium. The halide flux deoxidation using Ca and the molten  $\text{CaCl}_2$ <sup>20,21</sup> could successively deoxidize Ti to an oxygen level below that obtained by the Ca deoxidation, and its application to Nd-magnet seems attractive.

The purpose of this work is to examine experimentally the applicability of both Ca reduction and Ca deoxidation from the Nd-magnet scraps towards the preparation of low oxygen material which can be served for melting. The separation of Ca contamination after oxygen removal was also studied using the leaching in the aqueous solutions.

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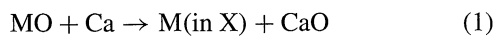
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## 2. Concept and Requirements

### 2.1 Thermodynamics of Ca reduction and deoxidation

Ca reduction from the oxides MO such as  $\text{Nd}_2\text{O}_3$  or  $\text{FeNdO}_3$  is expressed as,



where the reduced metal (M) dissolves in the Nd-magnet (X). The free energy change for chemical reaction (1),  $\Delta G_1^\circ$ , can be evaluated from the thermodynamic database.<sup>1,22)</sup> All the values  $\Delta G_1^\circ$  in case of  $\text{MO} = \text{Nd}_2\text{O}_3$ ,  $\text{FeNdO}_3$ ,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  are negative, if M is pure. The smaller activity of M than unity due to dissolution of M into X can enhance the reaction (1) further. This reflects the experimental evidences that Ca could reduce these oxides reported in the scraps.<sup>2,3)</sup>

The principle of Ca deoxidation and its applicability to the Nd-magnet (X) will be given here.<sup>16,20,21)</sup> Both in Ca-deoxidation and in halide flux deoxidation, the dissolved oxygen in X is removed commonly as,



$$\ln[\text{mass\%O in X}] = \frac{\Delta G_2^\circ}{RT} + \ln \frac{a_{\text{CaO}}}{a_{\text{Ca}} \cdot f_{\text{O in X}}} \quad (3)$$

where  $\Delta G_2^\circ$  is the free energy change for eq. (2),  $a_{\text{Ca}}$  and  $a_{\text{CaO}}$  are the activity of Ca and CaO, respectively.  $[\text{mass\%O in X}]$  is the equilibrium concentration of oxygen (mass%) in X, and  $f_{\text{O in X}}$  the Henrian activity coefficient of oxygen in M relative to 1 mass%O. When Ca and CaO coexist, for example, in the binary system at 1273 K,  $a_{\text{Ca}}$  and  $a_{\text{CaO}}$  were assessed as 0.991 and 1.00, respectively.<sup>16)</sup> This reflects the case of Ca deoxidation under the Ca–CaO equilibrium.

Halide flux deoxidation decreases  $a_{\text{CaO}}$  in eq. (3), while  $a_{\text{Ca}}$  is kept nearly unity and  $f_{\text{O in M}}$  constant. Enough amount of the by-product CaO can dissolve in  $\text{CaCl}_2$ , because the solubility of CaO in  $\text{CaCl}_2$  is about 21 mol%CaO at 1273 K.<sup>23)</sup>  $a_{\text{Ca}}$  of metallic Ca decreases only a little in ternary Ca–Cl–O system, because the equilibrium solubility of  $\text{CaCl}_2$  in the molten Ca can be neglected,<sup>24)</sup> and because that of Ca in the molten  $\text{CaCl}_2$  is about 6 mol%Ca.<sup>25,26)</sup> This halide flux deoxidation is experimentally proved that Ca holds enough reducing ability when Ca is saturated in  $\text{CaCl}_2$ , and that the halide flux deoxidation is more intensive than the deoxidation under Ca–CaO equilibrium.<sup>16,20,21)</sup>

The mechanism is speculated as following. The reductant Ca attaches to the sample surface and the layer of by-product CaO surrounds the sample during reduction or deoxidation.<sup>4,27)</sup> This CaO layer adhered to the deoxidized material is removed by dissolution in  $\text{CaCl}_2$ , and the subsequent deoxidation by Ca is enhanced because of lack of CaO layer.<sup>28)</sup> Practically the mixing of  $\text{CaCl}_2$  even in a few percent was effective to dissolve the residual Ca and CaO into the aqueous solution.<sup>5,28)</sup>

The by-product CaO and  $\text{CaCl}_2$  can be removed by leaching in the acidic aqueous solution or the other solutions such as  $\text{NH}_4\text{Cl}$ .<sup>27)</sup> Note that CaO transforms to the hydrate and that  $\text{Ca}(\text{OH})_2$  can dissolve below  $\text{pH} < 11$ .<sup>1)</sup>

### 2.2 Application to Nd-magnet

The Nd-magnet (X) consists mainly of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  magnetic phase, Nd-rich phase and B-rich phase ( $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ ). Because the thermodynamic data of oxygen in these phases,  $f_{\text{O in X}}$ , were not known, it is impossible to predict quantitatively to what oxygen content Ca can deoxidize the Nd-magnet. No thermodynamic data was found for a possible oxide  $\text{NdBO}_3$ ,<sup>3)</sup> and the chemical formula of the resin, machine oil or plastic coating materials in the scraps were unknown or dependent on the lots. We assume, however, that  $\text{NdBO}_3$  and these organic substances can be also reduced by the strong reductant such as Ca.

The reactivity of Ca with Nd will be studied, although Fe does not react with Ca. When the extra amount of Ca is applied for reduction of  $\text{Nd}_2\text{O}_3$ , it may form Nd-rich Ca liquid alloy (eutectic composition is 23.4 mol%Ca at 1165 K in the Nd–Ca binary phase diagram<sup>29)</sup>) or Nd–4.1 mass%Ca solid solution.<sup>4)</sup> Nd metal reduced by Ca is generally avoided as the starting materials for Nd-magnet, because the residual Ca in the magnet weakens the magnetic properties. This impurity Ca, however, can be lowered in RD process. Takeya *et al.*<sup>5,6)</sup> reported that the magnet by RD process using Ca was contaminated of only 0.07 mass%Ca, and that 1.01 mass%Ca segregated at the grain boundaries. In case of oxidized scraps,  $\text{Nd}_2\text{O}_3$  may isolate from the bulk, and the Nd diffusion into the matrix may delay. Once the excess amount of Ca formed the Nd–Ca alloy,<sup>4,30)</sup> this Nd–Ca alloy may dissolve into the aqueous solution. It causes the Nd loss from the recovered scraps. We assume that the final separation of Ca and the compositional control can be done in melting after oxygen removal, although Ca contamination should be minimized before melting. The excess Ca and the by-product CaO will be separated in the acid aqueous solutions after oxygen removal.

The gaseous Ca can remove oxygen thermodynamically as well as liquid Ca. Practically Ca as liquid or gas can react as reductant above the melting temperature.<sup>4,27)</sup> The equilibrium vapor pressure of Ca is about 200 Pa at the melting temperature of Ca, 1112 K,<sup>1,22)</sup> and it becomes higher at the higher temperature. Ca vapor may leak out from the reacting hot zone if the pressure becomes too high. The vapor pressure below 1273 K is practically high enough to react as the vapor.<sup>4,27)</sup> Note that the evaporation of the molten  $\text{CaCl}_2$  can be suppressed well below 1600 K.<sup>1,22)</sup> Considering the temperature endurable for the reacting vessel, the maximum temperature for oxygen removal was set as 1223 K.

Adjusting the requisites to avoid the side reactions, we may choose Ca vapor as the reductant source. Ca vapor does not contaminate the magnet. Namely, carbon is one of the major impurities in Ca, and carbon is also one of the elements that should not enter in the Nd-magnet to keep good magnetic properties.<sup>2)</sup> When Ca vapor is applied, carbon is trapped in Ca liquid and carbon does not touch with the Nd-magnet.

This work examines, therefore, the applicability of (1) Ca vapor, (2) Ca liquid, and (3) Ca vapor+ $\text{CaCl}_2$  melt, for reduction and deoxidation. The coreduction from the oxide mixture will be reported separately in connection with carbon removal in Part I.<sup>2)</sup> Here the starting materials are the scraps oxidized slightly as  $\text{Nd}_2\text{O}_3$ , or the scraps consisting mainly of  $\text{Nd}_2\text{O}_3$  and  $\alpha\text{-Fe}$ .<sup>3)</sup>

Secondly, we should choose experimentally the efficient

Table 1 Starting materials used in this work.

	Chemical composition (mass%)									Grain size
	Nd	Pr	Dy	Fe	B	Co	Mo	O	C	
Powder A	29.2	0.07	4.71	Bal.	1.2	3.35	3.12	0.57	0.08	>0.5 mm < 1.5 mm
Powder B	19.5	4.86	2.36	Bal.	0.84	0.08	<0.01	5.6	1.3	about 1 $\mu$ m
Powder C	19.2	5.35	3.30	Bal.	0.89	0.83	<0.01	10.9	0.017	about 0.01 mm

aqueous solution that can remove the residual Ca and the by-product CaO. The calcium components can be separated in the acidic solution, while the reduced Nd may dissolve easily into such acid solution if pure Nd or Nd–Ca alloy is formed by reduction. We will select experimentally the optimum condition that Ca is removed from the scraps but that Nd remains in the scraps.

### 3. Experimental

Table 1 shows the chemical composition of the powder scraps served to this work. The metallic components were chemically analyzed by using inductively coupled argon plasma-atomic emission spectrometry (ICP-AES), and oxygen and carbon were analyzed by using LECO TC-336 and LECO CS-444 analyzer, respectively.

“Powder A” was obtained from the scraps in the industrial sintering process. The sintered magnet scraps were crashed and separated to be a grain size of about 1 mm. “Powder B” was the powder obtained during machinery operation, where the cutting oil and water was industrially fed. “Powder B” is also used in our separated study, Part I.<sup>2)</sup> “Powder C” was oxidized in vacuum for carbon removal. The details of carbon removal from these scraps were described in Part III.<sup>3)</sup>

Figure 1 shows the experimental arrangements for deoxidation. Three trays made of pure Mo foils were settled in the stainless steel vessel locked by the screws. For deoxidation by Ca vapor, Ca (> 99% metallic purity) granules of a few mm in diameter were set on the lower tray, and the sample powder was laid on the two upper trays. For the deoxidation by Ca liquid, Ca granules were mixed with the sample powder and this mixture was divided on these three trays. In case of CaCl<sub>2</sub> addition, CaCl<sub>2</sub> (99.9%, anhydrous) was mixed with the sample powder and this mixture was put on the upper two trays, while the Ca grains were separately placed on the lower tray. For Powder C, the mixture of Ca, CaCl<sub>2</sub> and the sample powder was placed on the three trays.

Table 2 listed the experimental conditions for deoxidation. The charged amount of Ca was normally three to five times larger than the theoretical necessity, considering leakage of Ca vapor from the vessel. The amount of CaCl<sub>2</sub> for Run #4 was determined, assuming that the whole oxygen was removed as CaO and that this amount of CaO could be dissolved to 19 mol% in the CaCl<sub>2</sub> melt.<sup>23)</sup> For Run #5, the major part of CaO cannot be dissolved because only a small amount of CaCl<sub>2</sub> was added.

The stainless steel vessel was tightened between the two

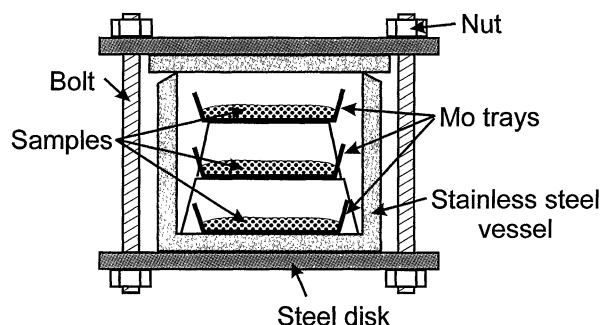


Fig. 1 Schematic illustration of the reaction vessel for deoxidation by calcium.

disks, subsequently evacuated at 873 K, heated in an Ar gas flow and cooled in the furnace.

After heat treatment, Ca, CaO and CaCl<sub>2</sub> were separated from the specimens under supersonic vibration with either the distilled water, HCl, KOH, or H<sub>3</sub>PO<sub>4</sub> aqueous solutions. pH was measured by the digital pH meter calibrated by several solutions. The powders after leaching were rinsed by water and dried in vacuum at 343 K for several hours, and served to chemical analysis, SEM (Scanning Electron Microscopy) observations, EDX (Energy Dispersive X-ray) analysis and XRD (X-ray diffraction) measurements.

### 4. Result and Discussion

#### 4.1 Solution choice for calcium removal

Ca vapor was applied to “Powder A” (listed as #1 in Table 2). The white CaO covered the sample after holding at 1223 K for 39.6 ks. The as-deoxidized sample was divided into 4 parts, and each part of 20 g was independently leached by 10<sup>−4</sup> m<sup>3</sup> solution selected from the distilled water, HCl aqueous solution with pH = 4, KOH aqueous solution with pH = 9 or 11. Subsequently the powders were rinsed in the distilled water for 1.8 ks, and dried in vacuum.

Figure 2 shows the concentration of the leaching solutions when the leaching time was 600 s. Figures 3 and 4 shows the composition and the mass loss of the powders after leaching, respectively. The residual Ca and the by-product CaO could dissolve efficiently into the acidic HCl solution (pH = 4). However, the Nd, Dy and Fe were also leached, because these elements can dissolve as anions in the aqueous solution, judging from electrochemical potential diagrams.<sup>1,31)</sup> In the basic KOH solutions (pH = 9 and 11), the elimination of these elements was well suppressed as shown in Figs. 2–4. When

Table 2 Experimental conditions for oxygen removal.

Run	Starting materials		Reductant and flux		Heat treatment
		Charged mass		Charged mass	
#1	Powder A	100 g	Ca vapor	7.5 g	1223 K, 39.6 ks
#2	Powder B	50 g	Ca vapor	12.5 g	1223 K, 50.4 ks
#3	Powder B	50 g	Ca liquid	12.5 g	1223 K, 50.4 ks
#4	Powder B	50 g	Ca vapor +CaCl <sub>2</sub>	12.5 g Ca +21 g CaCl <sub>2</sub>	1223 K, 50.4 ks
#5	Powder C	50 g	Ca liquid +CaCl <sub>2</sub>	13.5–33.8 g Ca +2.5 g CaCl <sub>2</sub>	1173 K, 3.6 ks

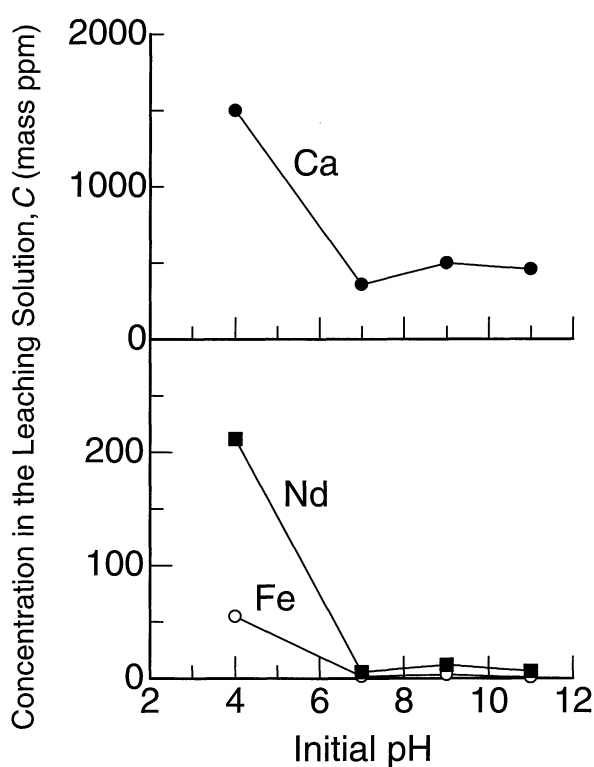


Fig. 2 Concentration of metallic elements in the leaching solutions.

the recovered mass and the concentration of (Nd + Dy) were used, the yield of (Nd + Dy) recovery was evaluated as 84% for the leaching in the acid solution (pH = 4), and about 90% for the other solutions. This Nd loss was mainly due to the fine particles that we could not recover from the solution.

It was difficult to remove the residual Ca and CaO from the scrap powder within a limited period of 600 s, although we had expected that CaO could be leached even in the basic solutions. The Ca concentration in the as-deoxidized powders (before leaching) was analyzed as 1.5 mass%. The theoretical mass loss after CaO elimination is evaluated as 1.97% and indicated as the broken line in Fig. 4. About 8% mass loss is, however, deduced from the (Nd + Dy) recovery, if we take into account that 10% scraps was lost as fine particles. About 0.6 mass%Ca remained in the sample when KOH solutions were used as shown in Fig. 3. EDX analysis showed that the residual calcium existed in some contents as CaO, Ca(OH)<sub>2</sub> or some hydrated hydroxides due to the slow dissolution into

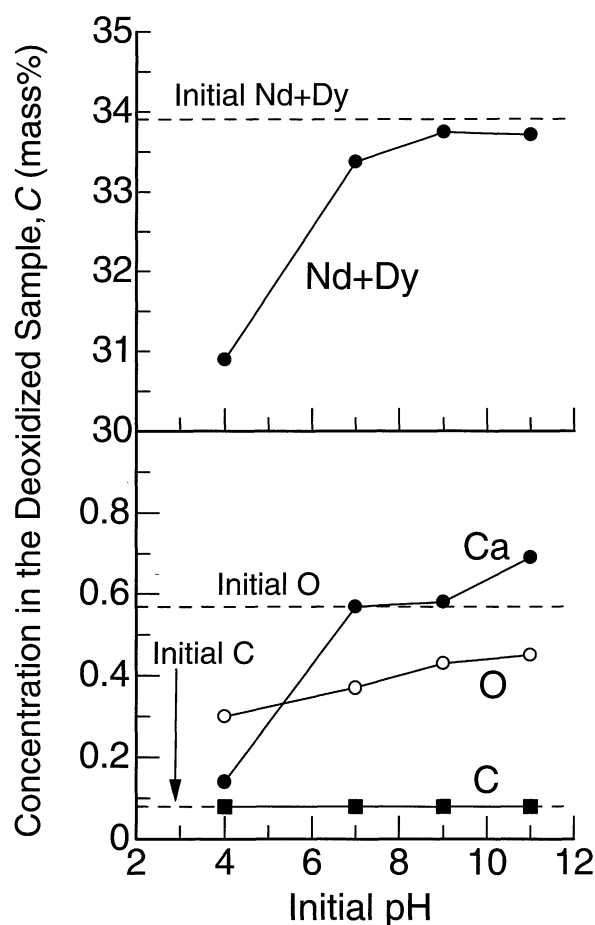


Fig. 3 Composition of the deoxidized sample #1 after leaching.

basic water. This is one of the reasons that the mass loss was only about 1% as shown in Fig. 4. The attempts of Ca leaching in the prolonged time will be reported in the next section.

Oxygen in CaO, Ca(OH)<sub>2</sub> or some hydrated hydroxides is counted as the analytical values, but the whole oxygen in the samples were analyzed as about 0.4 mass%O. This is in an allowable level for the subsequent melting. Carbon concentrations were independent of the experimental conditions, and identical with the starting value. Carbon removal was not found in Ca deoxidation process, therefore, it was judged that the treatment for carbon removal was needed prior to Ca deoxidation, as described in Part I.<sup>2)</sup>

It may conclude that the acid solution leached some

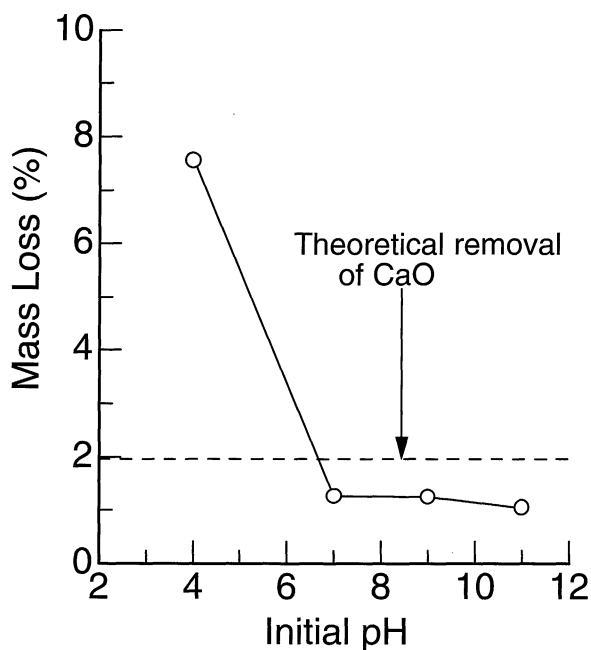


Fig. 4 Mass loss of the deoxidized sample #1 after leaching.

amounts of Nd. Ca leaching was not effective in the basic solutions. Therefore, the water of pH = 7 was taken for leaching in the further study. This is partially because no usage of the specialized leaching solution becomes an economical advantage.

#### 4.2 Calcium removing process

The slightly oxidized "Powder B" were deoxidized by Ca liquid, Ca vapor or Ca vapor + CaCl<sub>2</sub> flux. After deoxidation, XRD identified that the samples reacted with Ca liquid or Ca vapor were covered by CaO and Ca. The sample reacted with Ca vapor + CaCl<sub>2</sub> flux was black and adhered heavily to the Mo tray. EDX analysis showed that it consisted of the magnet sample, Ca and CaCl<sub>2</sub>. In the as-deoxidized state of these samples, it was difficult to identify the trace of Nd–Ca liquid alloy by XRD and EDX.

50 g samples were leached at room temperature by 10<sup>-3</sup> m<sup>3</sup> of the distilled water, or the 10% H<sub>3</sub>PO<sub>4</sub> buffer solution of pH = 7.0. These leaching solutions were exchanged every 300 s, and pH of the used solutions were measured after separating the sample powder. In the first 300 s, pH increased rapidly to 12 as shown in Fig. 5. Accompanied with a strong exothermic reaction and hydrogen evolution due to dissolution of Ca metal, pH then decreased gradually. The approach to pH = 7 was slowest for the sample deoxidized by Ca liquid, because more amount of the residual Ca was attached to the sample. The decrease of pH was the fastest for the sample deoxidized with CaCl<sub>2</sub>.

The constant pH could not be maintained in the distilled water because of quick dissolution of Ca. The buffer solution was studied because the dissolution of CaO may be enhanced by keeping pH lower.

When the buffer solution of pH = 7 was used, the increment of pH was suppressed as shown in Fig. 6. The leaching time shortened because the dissolution rate of CaO or Ca(OH)<sub>2</sub> becomes faster in the region of lower pH.

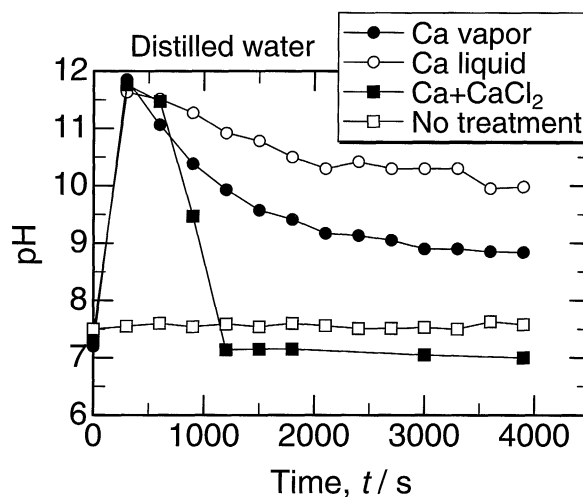


Fig. 5 Change of pH during leaching in the distilled water.

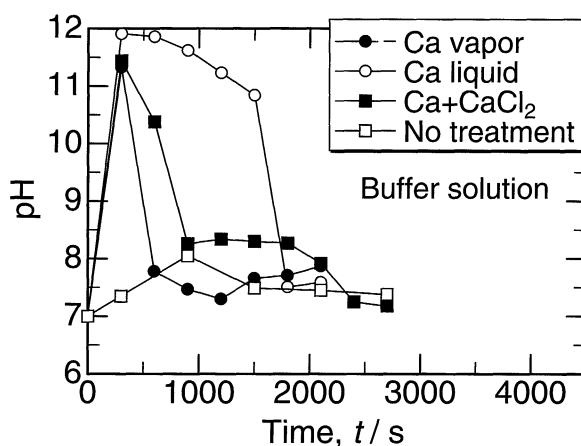


Fig. 6 Change of pH during leaching in 10 vol% H<sub>3</sub>PO<sub>4</sub> aqueous solution.

#### 4.3 Choice of calcium deoxidizer

Table 3 lists the chemical compositions after the final rinsing of "Powder B" which were deoxidized by Ca vapor (#2), Ca liquid (#3) and Ca vapor + CaCl<sub>2</sub> flux (#4). For comparison, the initial powder that no Ca deoxidation was applied was similarly leached by the same solutions.

The rare earth components (RE) consisting of Nd, Pr and Dy were not changed either by Ca vapor deoxidation or by Ca liquid deoxidation. The Ca content in the sample as-deoxidized by the Ca vapor (#2) was lower than the other two methods. In case of the strongly oxidized magnet such as "Powder B", the Ca vapor could not supply enough amount of Ca into the powder sample within the experimental time, and the oxygen concentration after CaO removal remained as high as the initial powder. Note that the grain size of Powder B was finer than that of Powder A. It is considered, therefore, that the thick CaO layer covering the sample prohibited from the subsequent reaction with Ca vapor. Industrial application of Ca vapor deoxidation seems difficult because of this slow kinetics when the charge became larger.

The Ca liquid deoxidation could decrease the oxygen concentration, although the removal of Ca components was not perfect under the applied conditions, as shown Ca concentration in Table 3 (#3). Although the analytical oxygen was as

Table 3 Analyzed compositions for the powder B deoxidized at 1223 K for 50.4 ks.

Deoxidization methods	Leaching Solutions	Composition (mass%)			
		RE	Ca	O	C
No treatment (Initial powder)	Before leaching	26.72	<0.01	5.6	1.3
	Distilled water	27.21	0.01	5.1	0.7
	Buffer solution	26.22	0.01	6.9	0.61
Ca vapor (Run #2)	Before leaching	28.74	1.00	—	—
	Distilled water	28.13	0.02	7.0	0.08
	Buffer solution	28.04	0.26	7.3	0.11
Ca liquid (Run #3)	Before leaching	23.84	5.69	9.7	0.28
	Distilled water	28.67	1.42	2.91	0.28
	Buffer solution	28.03	3.05	4.2	0.34
Ca + CaCl <sub>2</sub> (Run #4)	Before leaching	17.01	5.55	4.5	0.03
	Distilled water	4.30	0.04	0.99	0.09
	Buffer solution	4.13	0.08	1.0	0.1

high as 3.0 mass%, oxygen in the magnetic phase is calculated as a value lower than 2.3 mass%O, considering oxygen as CaO or Ca(OH)<sub>2</sub>.

The addition of CaCl<sub>2</sub> (#4) was significantly effective for removal of calcium and oxygen during the leaching, as shown in Table 3. The hydrogen gas evolution during the leaching suggested that a fairly large amount of Ca dissolved in the mixture. However, the concentration of rare earth elements (RE) in the sample was also significantly lower than the other two methods. This reason is still not clear, because the solubility of RE in CaCl<sub>2</sub> melt was not known. Another possible explanation of RE dissolution into the aqueous solution is as follows.

The main oxygen sources in “Powder B” are the oxides of RE and the organic substances.<sup>3)</sup> Assuming that RE<sub>2</sub>O<sub>3</sub> in “Powder B” could be reduced to metallic RE or Ca–RE liquid alloy, the handling of the RE precipitates or Ca–RE alloy in the aqueous solution might cause the oxidation and hydration of RE. When CaCl<sub>2</sub> dissolved CaO, pH approaches toward 7 in a shorter time because the leaching of CaCl<sub>2</sub> + CaO is faster than that of pure CaO, as shown in Figs. 5 and 6. Further repeated leaching in the range of pH = 7 causes the dissolution of RE or Ca–RE alloy, because the RE hydrates in the basic aqueous solution, and because Nd(OH)<sub>3</sub> can dissolve in pH < 8.<sup>31)</sup> The analytical oxygen concentration decreases if the formed Nd(OH)<sub>3</sub> disappears. Unfortunately, no direct evidences of the formation of metallic RE or Ca–RE liquid alloy could not be obtained by either EDX or XRD analysis, because of heavy Ca contamination in the as-deoxidized samples, and because of less crystalline state of Nd(OH)<sub>3</sub>.

Some amounts of carbon was removed by rinsing in the distilled water without any heating. It was because the attached organic substances such as machinery oil were partially separated.

Thermodynamically NdC<sub>2</sub> is more stable than CaC<sub>2</sub>,<sup>1)</sup> and it is difficult to remove carbon as CaC<sub>2</sub>. The residual organic materials would be burned during heating and leaked out as CO<sub>2</sub> gas from the vessel. The detailed study on carbon removal is reported in Part III.<sup>3)</sup> Carbon content in case of Ca liquid deoxidation was a little higher than those by the other two methods. It was because impurity carbon in the Ca liquid

contaminated the Nd-magnet. The allowable level of carbon could not be obtained by our three methods. Therefore, the carbon removal treatment is conducted prior to oxygen removal.<sup>2,3)</sup>

Summarizing briefly the results obtained above, Ca liquid deoxidation was fit for industrial application. The addition of CaCl<sub>2</sub> enhanced to dissolve the by-product CaO into the aqueous solution, but too much addition caused the problems.

#### 4.4 Calcium deoxidization after carbon removal

Considering practical application, the lower temperature, the shorter time, the less amounts of CaCl<sub>2</sub> and Ca, and the higher yield are desired. “Powder C” (as decarbonized as reported in Part III<sup>3)</sup>) was served to the oxygen removal by calcium. The experimental condition was listed in Table 2. The cooled samples were broken into pieces for 7.2 ks in water, and repeatedly leached in the distilled water. The solution was controlled so that pH maintained not below 11. The fine powder in the scraps was lost during the repeated leaching and decantation, and the mass loss was about 25–60%.

Figure 7 shows the chemical compositions after the final rinsing of “Powder C”. Oxygen was well removed to be about 0.7 mass%, although the samples were deoxidized only for 3.6 ks. When the amount of calcium 1.5 times larger than the stoichiometric amount was charged, the analytical oxygen level became constant, where both the residual calcium and the elimination of rare earth components were minimized. The kinetics for deoxidation and the improvement of sample recovery should be pursued more in detail, however, the oxygen level could be below 1 mass% even from the heavily oxidized samples. This result encourages us to develop further this deoxidation method for industrial recycling.

## 5. Conclusions

Powder scraps of Nd–Fe–B magnet were deoxidized by using gaseous Ca, liquid Ca or Ca–CaCl<sub>2</sub> equilibrium at 1223–1273 K. The deoxidized samples were leached by the distilled water or some aqueous solutions. When pH decreased to about 8 after several times leaching, the oxygen and calcium concentration in the samples were below 0.4 and

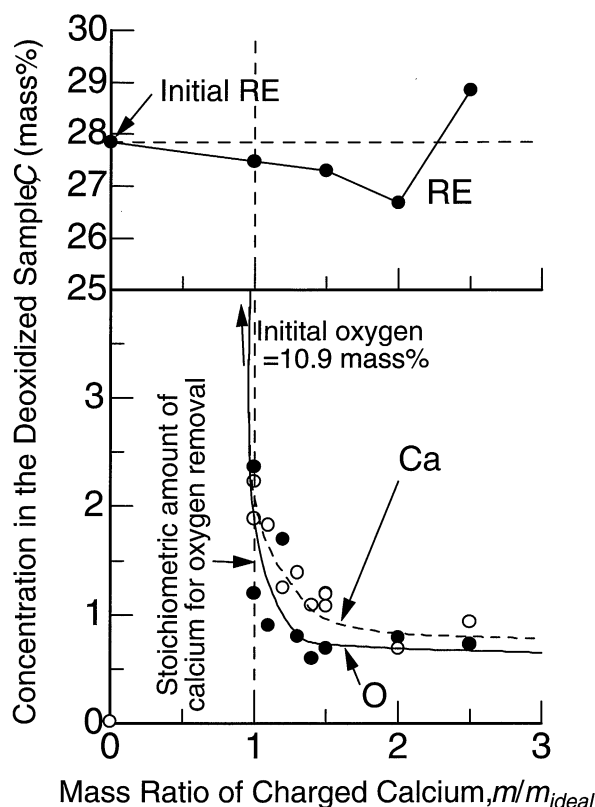


Fig. 7 Concentrations in the deoxidized samples #5 after leaching, where the charged amount of calcium is normalized by the stoichiometric amount,  $m_{ideal}$ .

0.7 mass%, respectively, and the removal of rare earth elements was minimized. Ca vapor deoxidation could not supply enough amount of Ca through CaO layer. When plenty of  $\text{CaCl}_2$  was added, the dissolution rate of CaO into the aqueous solution was faster, but some parts of rare earth components also dissolved.

A useful combination for industrial application is the deoxidation by liquid Ca + small amount of  $\text{CaCl}_2$  and the subsequent leaching in water controlling  $\text{pH} > 8$ . Oxygen in the heavily oxidized scraps (Powder C) could be removed to 0.7 mass%, while no rare earth components were eliminated.

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