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# Extraction and recovery characteristics of Fe element from Nd–Fe–B sintered magnet powder scrap by carbonylation

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#### Abstract

Iron element was extracted from the powder scrap of Nd–Fe–B sintered magnets *via* the carbonylation reaction with sulfur as a catalyst. The resultant carbonyl complex was Fe(CO)<sub>5</sub> and the yield was evaluated to be ~56% by energy dispersion X-ray analysis. After applying the hydrogenation disproportionation treatment on the powder scrap, the extraction rate for Fe element was considerably accelerated on the resultant  $\alpha$ -Fe/Fe<sub>2</sub>B/NdH<sub>2</sub> (or neodymium oxides) nanocomposite powders to produce Fe(CO)<sub>5</sub> in a maximum yield of ~92%. © 2007 Elsevier B.V. All rights reserved.

Keywords: Recycling; Nd-Fe-B sintered magnet scrap; Hydrogen disproportionation; Carbonylation; Iron pentacarbonyl

## 1. Introduction

Since the Nd-Fe-B sintered magnets were invented by Sagawa et al. [1], they have been developed to functional types or shapes of the high-performance permanent magnets and used as various application products such as voice coil motors (VCMs) for hard disk drives, magnetic field sources of MRI, driving motors for hybrid-type electric vehicle and so on, due to their superior magnetic properties to Alnico or ferrite magnets. Consequently, the Nd–Fe–B sintered magnets occupy the largest share in the hard magnet market total, and the production amount per year has currently become more than 30 kt in the world. However, about 25% of such sintered Nd-Fe-B alloy materials are wasted as useless scraps in manufacturing processes, e.g. sintering, cutting/polishing, magnetizing and so on. The sintered magnet scraps are mainly classified into two types: one is the bulk-type scrap which may be reused as a part of raw alloy materials for producing the Nd-Fe-B sintered magnets because the oxygen content of such cracked magnets is usually small (<0.5 wt%). Other is the fine powder scrap which is difficult to reuse directly as magnet components, and this is because that it is heavily oxidized for the strong oxygen affinity of rare earth metals (see Table 1). The major part of such magnet scraps is

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produced as the fine powder generated in the cutting and polishing processes to fit the sizes demanded for application products, so that these kinds of scraps account for  $\sim$ 80% of total Nd–Fe–B sintered magnet scrap.

A number of studies have been made to propose the recycling processes on the above powder scrap [2–9]. In our previous works, the hydrogenation disproportionation (HD) treatment [10] on the powder scrap has been found to be effective for reusing the Nd–Fe–B powder scrap as good electromagnetic wave absorbers in a GHz range [7].

In an industrial scale, rare earth components in the powder scrap are dissolved in aqueous solutions of hydrochloric or nitric acid, and subsequently isolated *via* the precipitation by complexing with oxalic acid. After further mutual separation among the rare earth components, Nd, Pr or Dy resultantly is reused as the individual rare earth component for Nd–Fe–B sintered magnets. However, this is the problem that one has a large amount of the scrap residue mainly including of Fe and B as industrial wastes, since the recycling cost of Fe dose not meet the market price and B is a poisonous element to be controlled environmentally.

On the contrary, it is well known that carbonylation reaction has been applied to extract or purify transition metals. For example, highly pure nickel metal is produced from the crude nickels through the carbonylation that is known as Mond process [11]. In a similar manner like this, Fe(CO)<sub>5</sub> is formed with CO gas under high-pressure condition and such carbonylation is generally catalyzed with chalcogen elements as catalysts [12].

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Table 1 Typical composition of the Nd–Fe–B powder scrap

Elements	wt%
Nd	23.4
Dy	4.1
Fe	62.3
Co	3.2
0	5.1
В	0.9

In this study, the above-carbonylation reaction was applied to Nd–Fe–B sintered magnet powder scrap to concentrate the rare earth elements by extracting the Fe component. The feasibility for efficient recycling process for the above scrap was studied by optimizing the material and reaction conditions.

#### 2. Experimental

The Nd–Fe–B sintered magnet powder scrap was provided by some magnet companies. The Nd–Fe–B sintered magnet powder scrap with typical composition (see Table 1) was used in the present study. An appropriate amount of the powder scrap (1 g) was put into a stainless steel autoclave vessel of 50 ml (Nitto koatsu Co. Ltd.), together with a small amount of sulfur powder as a catalyst for carbonylation, and then carbon monoxide was charged up to 1.9 MPa at 25 °C after evacuating it. Meanwhile, a part of the powder scrap was decomposed by oxidizing at 250–300 °C for 6 h in air or hydrogenating at 600 °C for 4 h in H<sub>2</sub> (HD powder) in order to precipitate the  $\alpha$ -Fe phase as Fe/Fe<sub>2</sub>B/Nd<sub>2</sub>O<sub>3</sub> nanocomposites, and then charged to the vessels with S and CO, respectively. The reaction conditions of carbonylation were 200 °C under 30 MPa for 24 h. After the reaction, carbon monoxide was purged through a decane trap. The residual solids were collected and washed with dehydrated hexane in a glove box circulated with a purified Ar gas.

The residual powders obtained after the carbonylation process were characterized by an X-ray diffractometer (RIGAKU, RINT2200) with a Cu K $\alpha$ radiation. Also, the atomic composition analysis was performed by an energy dispersive X-ray analyzer (HORIBA, EMAX EX-220SE) to evaluate the yield of iron carbonyl from the Nd/Fe metal ratio change before and after the carbonylation process. The product trapped in decane was analyzed by a FT-IR spectrometer (JASCO FT/IR-430). The surface area of the residual powders was measured by the conventional nitrogen adsorption method (BET).

### 3. Results and discussion

The conversion profiles from Fe metal to carbonyl compound on the as-obtained and HD-treated Nd–Fe–B powder scrap were shown as a function of sulfur content summarized in Fig. 1 (solid line) and the detailed values were listed in Table 2. The maximum conversion of 56% was obtained for the as-obtained Nd–Fe–B powder scrap when the sulfur catalyst concentration was 4 at.% with respect to the Fe content of Nd–Fe–B powder scrap. While increasing the sulfur concentration (>4 at.%), the conversion value was gradually decreased. This indicates that sulfur has a negative effect for the carbonylation of Fe metal in the higher concentration region.

The X-ray diffraction (XRD) patterns of Nd–Fe–B powder scrap before and after the carbonylation reactions are shown in Fig. 2(a)–(d). Peak patterns of the Nd<sub>2</sub>Fe<sub>14</sub>B phase were hardly changed by the carbonylation reaction, indicating that the Nd<sub>2</sub>Fe<sub>14</sub>B phase is stable under the above conditions and not suitable for the carbonylation. Hieber and Geisenberger [12]



Fig. 1. Concentration dependences of sulfur on the conversion to carbonyl for (a) the as-obtained Nd–Fe–B powder scrap and (b) hydrogenation disproportionated one.

have proposed that the carbonylation reaction of Fe metal proceeds *via* a FeS–CO intermediate complex, so that the reaction rate is considerably in the presence of sulfur. The low conversion for the as-obtained Nd–Fe–B powder scrap is also due to the low reactivity of S with the Fe element in the Nd–Fe–B lattice.

In order to enhance the reactivity of CO or S, the Nd–Fe–B phase was decomposed to fine powders by the oxidation or hydrogenation disproportionation (OD or HD) treatment. It has been reported for the OD treatment that the Nd<sub>2</sub>Fe<sub>14</sub>B phase was decomposed to  $\alpha$ -Fe, Fe<sub>2</sub>B and Nd<sub>2</sub>O<sub>3</sub> at 230 °C in oxygen as a following scheme [13]:

$$Nd_2Fe_{14}B + (O_2) \rightarrow Fe + Fe_2B + Nd_2O_3$$

The difference of oxygen affinity between Nd and Fe metals allows us to oxidize the rare earth element at proper heating tem-

Table 2

Iron conversion for the Nd–Fe–B powder scrap, oxidized one, and HD-treated one in the carbonylation with various chalcogen catalyst contents

Samples	Catalyst (at.%)	Conversion (%)
As-obtained	0	0
	1 (S)	55
	4 (S)	56
	7 (S)	55
	13 (S)	52
	19 (S)	31
	4 (Se)	50
Oxidization	4 (S)	58
Hydrogenation disproportion- ation (HD)	0	0
	1 (S)	88
	4 (S)	92
	7 (S)	88
	13 (S)	75
	19 (S)	68
	4 (Se)	90
Iron powder	7 (S)	90



Fig. 2. XRD patterns of (a) the as-obtained Nd–Fe–B powder scrap and the residual powders after the carbonylation with a various sulfur catalyst concentration of (b) 7 at.%, (c) 13 at.%, and (d) 19 at.%.

perature. Fig. 3(b) shows the XRD pattern of the scrap powder oxidized at 250 °C for 6 h in air. As expected, the  $\alpha$ -Fe phase was precipitated by oxidizing the Nd<sub>2</sub>Fe<sub>14</sub>B phase. The carbonylation reaction with 4 at.% of sulfur catalyst on the above-oxidized powder, however, gave the low iron conversion of 58%, which was almost the same in the case of the as-obtained scrap powder. As shown in Fig. 3(c), the peak intensity of  $\alpha$ -Fe(110) was weakened and the peaks assigned to Fe<sub>2</sub>O<sub>3</sub> were obviously observed after the carbonylation process. The oxygen content



Fig. 3. XRD patterns of (a) the as-obtained Nd–Fe–B powder scrap, (b) oxidized at 250  $^{\circ}$ C for 6 h, and (c) the residual powder after the carbonylation with 4 at.% of sulfur.

Table 3 Standard free energy and iron conversions for various iron compounds

Compounds	Catalyst (at.%)	$\Delta G^{\circ}$ (kcal/mol) at 200 $^{\circ}$ C	Conversion (%)
FeO	7 (S)	-115	0
Fe <sub>2</sub> O <sub>3</sub>	7 (S)	-110	0
FeB	7 (S)	-91	0
Fe <sub>2</sub> B	7 (S)	-81	0
FeS	0	-60	20

of the oxidized powder scrap was 11 wt%. Judging from the free energy of the formation of iron compounds (see Table 3), iron oxides such as FeO and Fe<sub>2</sub>O<sub>3</sub> are much stabler than FeS, suggesting that the FeS–CO intermediate through the carbonylation reaction is difficult to form on FeO or Fe<sub>2</sub>O<sub>3</sub>. Oxidization at 300 °C resulted in the further increase of oxygen content (13 wt%), and the iron conversion was also dropped to be 40%. This result supports the inhibition model on iron oxides mentioned above. The present oxidization disproportionation is not preferred as the pretreatment for carbonylation, because the fine powders of Nd–Fe–B powder scrap can be easily oxidized to generate iron oxide compounds.

Next, the HD treatment was performed on the above powder scrap as below [14,15]:

$$Nd_2Fe_{14}B + (H_2) \rightarrow Fe + Fe_2B + NdH_2$$

The diffraction pattern of the HD-treated powders (HD powder) was indexed as cubic  $\alpha$ -Fe as shown in Fig. 4(a). The diffraction patterns before and after the carbonylation reaction without a sulfur catalyst on the HD powder were almost the same as shown in Fig. 4(a) and (b), respectively. This result is similar to the case of the virgin powder scrap. When the sulfur content was increased up to 4 at.%, the diffraction peaks assigned to  $\alpha$ -Fe were disappeared, while the peaks of neodymium oxides (Nd<sub>6</sub>O<sub>11</sub> and Nd<sub>2</sub>O<sub>3</sub>) were newly emerged as seen in Fig. 4(c).



Fig. 4. XRD patterns of (a) the hydrogenation disproportionated Nd–Fe–B powder scrap (HD powder) and the residual powders after the carbonylation of (a) with a various sulfur catalyst concentration of (b) 0 at.%, (c) 4 at.%, (d) 13 at.%, and (e) 19 at.%.



Fig. 5. Time dependence of iron conversion on the carbonylation with 4 at.% of sulfur for the hydrogenation disproportionated Nd–Fe–B powder scrap (HD powder).

The carbonylation reaction on the HD powder with 4 at.% of sulfur catalyst gave the maximum iron conversion of 93% as shown in Fig. 1(b), which was also higher than that of the as-obtained powder scrap. These results bear out that the sulfur catalyst is essential to proceed the carbonylation reaction under the present conditions.

Fig. 5 shows the time dependence of iron conversion on HD powder carbonylated with 4 at.% of sulfur catalyst. The iron conversion was increased with time, and then the carbonylation of HD powder was saturated at 6 h. This saturated value may be the best conversion of iron component for the Nd–Fe–B sintered magnet scrap, because the FeB and Fe<sub>2</sub>B mixture compound that did not react on carbon monoxide confirmed from the supplemental experiments as shown in Fig. 6(a) and (b). Furthermore, as the standard free energy of formation for FeB and Fe<sub>2</sub>B was lower than FeS (Table 3), the iron conversion on the HD powder was limited due to the coexistence of iron boron compounds similar to that of iron oxides.

It has been reported that  $Nd_2Fe_{14}B$  was decomposed to form nano-sized lamellar structure [16], so the primary metal tissue size of iron (*t*) on the HD powder was calculated by the following Scherrer's formula:

$$t\,(\text{\AA}\,) = \frac{0.9\lambda}{\beta\cos\theta}$$

where  $\lambda$  is the wavelength of Cu K $\alpha$  radiation (1.5418 Å),  $\beta$  is the full width of half maximum of the peak, and  $\theta$  is the diffraction angle. By using the (1 1 0) peak of  $\alpha$ -iron phase in Fig. 4(a), the mean diameter of the iron particle was calculated to be ~20 nm. The nano-sized iron particles formed by the HD treatment are of high reactivity with carbon monoxide to show the highest iron conversion at the sulfur content of 4 at.%. As shown in Fig. 4 (curves (d) and (e)), the further addition of sulfur catalyst resulted in the formation of Fe<sub>1-x</sub>S (x>1), and the iron conversion gradually decreased with increasing the sulfur content. As a reference, the commercial FeS (purity: >99.9%)



Fig. 6. XRD patterns of (a) the commercial FeB and Fe<sub>2</sub>B reagents mixture, (b) residual powders after carbonylation on (a) with 7 at.% sulfur, (c) the commercial FeS, and (d) the residue powder after carbonylation of (c).

was reacted with CO under the same condition (without sulfur catalyst). After carbonylation, the FeS phase was completely changed to the Fe<sub>1-x</sub>S one (curves (c) and (d) in Fig. 6), and the iron conversion on it was only 20%. These results suggest that the formation of Fe<sub>1-x</sub>S phase retards the Fe(CO)<sub>5</sub> formation in carbonylation and the optimum sulfur concentration is around 4 at.%. These results were coincident with the previous study [12]. Other catalyst, selenium, as the same chalcogen element, was also applied to the carbonyl reaction process for HD powder. Similar catalyst concentration dependence was observed and the maximum iron conversion (~90%) was obtained at selenium concentration of 4 at.% (Table 2). Solid chalcogen is effective to catalyze the Fe(CO)<sub>5</sub> formation for the case of  $\alpha$ -Fe/Fe<sub>2</sub>B/NdH<sub>2</sub> nanocomposites.

The surface area of the HD powder was increased by the carbonylation reaction. The surface area values are 7 and  $38 \text{ m}^2/\text{g}$ before and after the carbonylation, respectively. This result indicates a selective extraction of Fe component by gaseous carbon monoxide. The large surface area is favorable for a subsequent rare earth element extraction by acid solvents such as nitric one and due to the increase of reaction contact area, allowing the rapid dissolution of rare earth elements.

The iron carbonyl complex produced by carbonylation was trapped by passing the CO gas into decane after the reaction. The color of decane solution was changed from transparent to yellow during the CO gas purging. Fig. 7(a) shows the FT-IR spectrum for the product trapped in decane. The absorption peak observed at 2009 cm<sup>-1</sup> was assigned to C=O stretching vibration. The reagent grade Fe(CO)<sub>5</sub> decane solution gave the same spectrum as shown in Fig. 4(b), and this solution showed the same color as the above solution trapped iron carbonyl. The iron carbonyl trapped in the decane solution was thermally decomposed at 200 °C. The EDX spectrum indicates that partially oxidized



Fig. 7. FT-IR spectra of (a) the product obtained by the carbonylation of hydrogen disproportionated Nd–Fe–B powder scrap (solid line) and (b) a commercial iron pentacarbonyl (dashed line).



Fig. 8. EDX spectrum of the iron powders derived from the extracted iron carbonyl complex.

iron powder was obtained and sulfur was not contained in the resultant iron carbonyl as shown in Fig. 8. This means that sulfur works only as a catalyst. Carbon element was originated from a carbon tape for fixing a sample. The XRD pattern of the thermally decomposed iron carbonyl shows only  $\alpha$ -Fe phase. From the above results, one can propose that the iron component in the Nd–Fe–B sintered magnet powder scrap was effectively extracted as iron pentacarbonyl with a high yield (>90%), indicating an effective reuse of an iron component from Fe-based powder scrap.

#### 4. Conclusions

The Fe element is effectively recovered as  $Fe(CO)_5$  via the carbonylation process on the Nd–Fe–B sintered magnet powder scrap under the presence of chalcogen catalysts like sulfur. The role of chalcogen catalyst is the activation of Fe metal, and CO gas may react with the partially chalcogenized surface of Fe metal particles. The nano-sized Fe metal particles with high surface area as derived from the hydrogenation disproportionation are desirable for the production of pure  $Fe(CO)_5$  at the industrial level.

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