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Effects of Dissolution Conditions on the Recovery of Neodymium Phosphate from Waste Magnets

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Abstract: Neodymium-iron-boron alloy ($Nd_2Fe_{14}B$) is used in the manufacture of magnets. Neodymium is one of the rare earth elements and is therefore valuable. Recovery, reuse, and recycling of rare earth elements is necessary to protect this rare earth resource. Recently, a new method for recovering neodymium phosphate from iron-neodymium mixture solutions using a two-step precipitation method has been reported, avoiding the difficulties reported with previous methods. In this method, iron compounds were removed in Step I and neodymium phosphate was precipitated in Step II. This novel phosphate process was proposed because rare earth phosphate is the main component of rare earth ores. In this study, we dissolved actual waste magnets in various acids to obtain neodymium phosphate by this two-step precipitation process. The resulting precipitates were evaluated by XRD (X-ray diffraction), infrared spectroscopy, color hue, UV-visible reflectance spectra, Fe/Nd ratio, and recovery of neodymium and iron. The results showed that neodymium phosphate was selectively obtained by using nitric acid and hydrochloric acid. In particular, samples prepared with nitric acid showedno reddening due to iron compounds.

Key words: Rare earth recovery, phosphoric acid, precipitation.

1. Introduction

Neodymium-iron-boron permanent magnets (typical formula; $Nd_2Fe_{14}B$) are used in hard disk drives, hybrid vehicle motors, and MRI (magnetic resonance imaging) devices [1, 2]. The production of such rare earth transition metal magnets generates a significant amount of scrap during the cutting process. Rare earth elements coexist with other rare earth elements in natural ores [3]. Many processes are required to separate the desired rare earth elements from other rare earth elements, and therefore, there is an industrial need to recover certain rare earths from scrap and other sources to save time and energy [4].

Rare earth elements are used in a variety of functional materials, but their supply to industry presents several problems [5, 6]. Rare earth ores are localized and generally contain actinides, which are radioactive elements [7]. Because mining rare-earth ores pose environmental problems, recycling rare earths from scrap and waste magnets may be a suitable alternative [8]. Several methods of rare-earth recycling have been reported. For example, solvent extraction using dilute ionic liquids can remove transition metals from rare earths [9, 10]. However, this process requires highly concentrated acids and special reagents. Alternatively, rare earths were recovered from magnetic alloy sludge by chemical vapor phase transport [11, 12]. However, this method requires high temperatures and special equipment. The shortcomings of these processes call for the development of new technologies to improve current recycling methods.

Rare earth phosphates, the main component of rare earth ores, are known to be stable in acidic and basic solutions [13]. Therefore, methods for obtaining rare earth metals from rare earth phosphates have been established and put into practical use. However, there are few reports on recycling processes using

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phosphoric acid. Precipitation is one of the most useful techniques for separating target metals from other metals [14, 15]. Precipitation methods using inorganic reagents are particularly convenient because they do not use harmful organic solvents. The wastewater generated by this process is also relatively easy to dispose of. The precipitation process can be easily estimated using laboratory simulated solutions. Metal hydroxides are often used in precipitation techniques because they can efficiently recover large amounts of metal cations [16, 17]. However, metal hydroxides are less selective in forming precipitates of the target metal in the presence of a precipitant.

In our previous study, we reported a new recycling process to recover neodymium phosphate from neodymium iron solutions using phosphoric acid [18]. This process is relatively simple and does not require the use of harmful organic solvents. Furthermore, a two-step precipitation method to recover rare earths as phosphates was investigated, and it was reported that iron ions are removed in Step I and neodymium phosphate can be obtained in Step II [19]. By this method, rare earth phosphates, the main component of rare earth ores, could be obtained without the use of high temperatures or special equipment. In step I, iron hydroxide was precipitated and removed, and then, as step II, phosphoric acid was added and the pH was adjusted with sodium hydroxide to precipitate neodymium phosphate. Although this new method requires more filtration operations, it has potential for practical application because it is a simple method involving only pH adjustment and filtration. Therefore, in this study, we dissolved actual waste magnets in various acids and attempted to recover neodymium phosphate using this two-step precipitation method.

2. Experimental Setup

2.1 Materials

All chemicals were of commercial purity (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and used without further purification.

2.2 Procedures

The flow of the experimental process is shown in Fig. 1. First, the waste magnet was heated at 400 °C for 1 h to remove the magnetic force. Then, the 100 or 200 mL of acid solution was prepared with a little excess amount of nitric acid, hydrochloric acid, and sulfuric acid to solve the following waste magnet. The waste magnet (3.2-3.6 g) was fed in these acid solutions for 2 days. These solutions were filtered to remove a small amount of undissolved residue. These solutions were adjusted to pH 4 using concentrated sodium hydroxide solution (step I) [19]. The formed precipitate was filtered and designated as “Precipitate I”. To the filtered solutions, 0.2 mol/L phosphoric acid was added so that P/Nd = 1/1. The amount of neodymium in the waste magnet was calculated according to a typical chemical formula, $Nd_2Fe_{14}B$. These filtered solutions were then adjusted to pH 7 using concentrated sodium hydroxide solution (step II). The formed precipitate was filtered as Precipitate II. Portions of the precipitates I and II were heated at 700 °C for 1 h and subjected to XRD (X-ray diffraction) analysis.

2.3 Analytical Methods

The crystalline phase composition of the precipitates and their thermal products was determined by XRD (MiniFlex, Rigaku Corp., Akishima, Japan) using monochromatic Cu Kα radiation (30 kV, 15 mA, 3°/min). IR (Infrared) spectra were measured on a Horiba FT-IR 720 spectrometer (Horiba Ltd., Kyoto, Japan) using the KBr disk method (Resolution: 4 cm^{-1}, 16 times scanned). To estimate the ratios of iron to neodymium in the precipitates, a portion of the sample was dissolved in a nitric acid solution. These ratios were calculated from the results obtained by Agilent 4200 MP-AES (Microwave Plasma Atomic Emission Spectroscopy). The color of the precipitates was estimated from the UV-Vis (ultraviolet-visible) reflectance spectrum (UV2100; Shimadzu Corp., Kyoto, Japan) (reference compound: $BaSO_4$). The color of the materials was also estimated using a

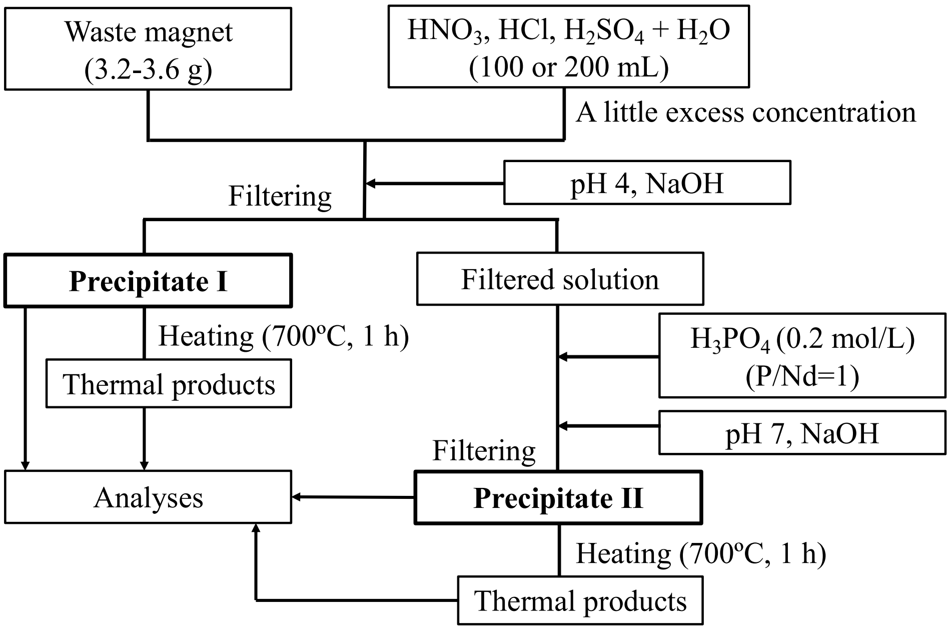

Fig. 1 Experimental procedure.

TES135 plus color analyzer (TES Electrical Electronic Corp, Taipei, Taiwan). The *L** value represents the whiteness of the material, with 100 corresponding to white and 0 to black. The *a** value represents the redness of a material, with positive and negative values representing red and green, respectively [19]. The *b** value indicates the intensity of yellow, with positive and negative values corresponding to yellow and blue, respectively.

3. Results and Discussion

3.1 Precipitate I

The precipitates produced in step I in this study were almost amorphous. This was based on the fact that it is difficult to crystallize because it is formed in an aqueous solution. Therefore, the heated ones were analyzed by XRD method to identify the compound. Fig. 2 shows XRD patterns of precipitates I heated at 700 °C. Precipitates I prepared with HNO_3 and HCl had the peaks of Fe_2O_3. These conditions were suitable for removing Fe ions from solution. The precipitate I prepared with sulfuric acid had unknown peaks in XRD pattern.

Fig. 3 shows UV-Vis. reflectance spectra of precipitates I prepared with various acid. Precipitate I prepared with sulfuric acid had the peaks at 523, 583, 680, and 743 nm, which were due to neodymium ions [20, 21]. This meant that the neodymium compound precipitated in step I when sulfuric acid was used for dissolution. Because the purpose of step I was to remove iron compounds and not precipitate neodymium compound, sulfuric acid was found to be unsuitable. On the other hand, the precipitates I formed using nitric acid or hydrochloric acid did not show the peaks due to neodymium compounds. This suggests that these precipitates do not contain much neodymium compounds.

Table 1 shows Fe/Nd ratios calculated from MP-AES results and recovery ratio in precipitates I. The recovery ratios of neodymium and iron are for reference only, since errors are likely to occur due to the small amount of sample measured. The recovery ratio of neodymium was high when 100 mL of sulfuric acid was used, however the cause was unknown. It was found that iron compound could be precipitated and removed under the condition using nitric acid. Under the conditions other than 100 mL of sulfuric acid, the

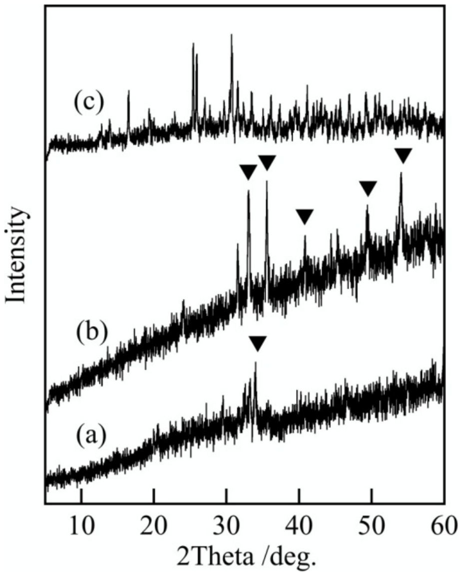

Fig. 2 **XRD patterns of precipitates I prepared with various acids (100 mL) and then heated at 700 °C, (a) HNO_3, (b) HCl, (c) H_2SO_4, ▼; Fe_2O_3.**

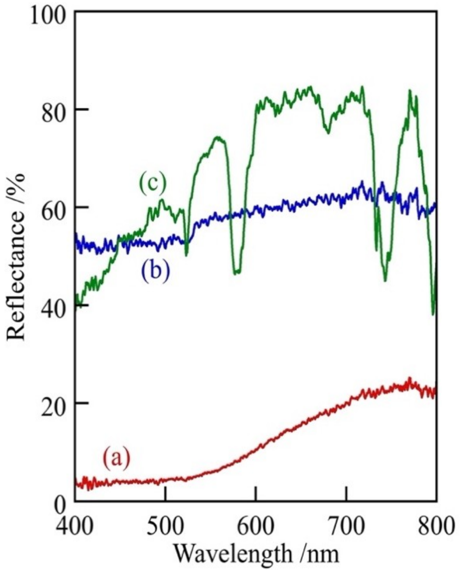

Fig. 3 **UV-Vis. reflectance spectra of precipitates I preparedwith various acids (100 mL), (a) HNO_3, (b) HCl, (c) H_2SO_4.**

Table 1 **Fe/Nd ratios calculated from MP-AES results and recovery ratios in precipitate I.**

Acid	Conc. (mol/L)	Volume (mL)	Fe/Nd ratio	Recovery Nd	Ratio/% Fe
HNO_3	2.0	100	40.28	15.56	87.97
HCl	2.0	100	120.85	0.07	1.17
H_2SO_4	1.0	100	0.09	67.46	0.83
HNO_3	1.0	200	70.23	6.81	67.50
HCl	1.0	200	177.38	0.03	0.76
H_2SO_4	0.5	200	46.88	0.10	0.67

Table 2 ***L****, ***a****, ***b**** **values of precipitate I.**

Acid	Conc. (mol/L)	Volume (mL)	*L**	*a**	*b**
HNO_3	2.0	100	36.41	19.13	11.28
HCl	2.0	100	41.01	7.04	9.82
H_2SO_4	1.0	100	80.75	6.15	12.04
HNO_3	1.0	200	33.25	17.69	14.71
HCl	1.0	200	44.29	13.67	14.66
H_2SO_4	0.5	200	54.27	12.82	21.65

precipitates I exhibited a high Fe/Nd ratio, indicating that iron compounds could be selectively removed. The precipitate becomes reddish brown when the proportion of iron (III) hydroxide is high. Table 2 shows *L**, *a**, *b** values of precipitate I. The *L** values corresponding to lightness are low, while the *a** values corresponding to redness are positive. The results of *L**, *a**, *b** values also showed that conditions other than 100 mL of sulfuric acid were suitable.

3.2 Precipitate II

When not heated, precipitate II was nearly amorphous. Therefore, the XRD patterns of precipitate II heated at 700 °C for 1 h are shown in Fig. 4. All precipitates II showed a peak pattern of $NdPO_4$. Strong peaks were observed in the XRD pattern of precipitate II prepared with hydrochloric acid. Fig. 5 shows IR spectra of precipitates II prepared with various acids.

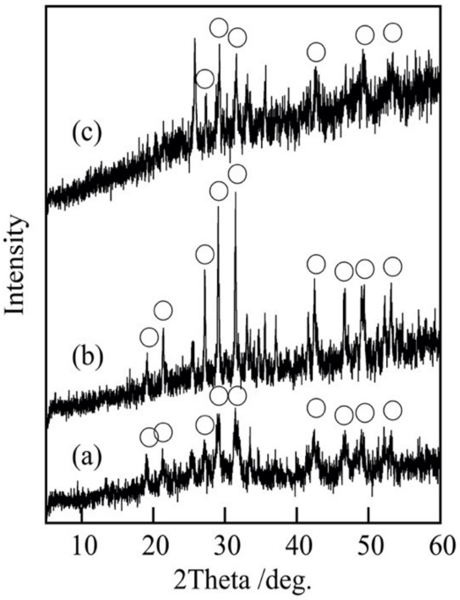

Fig. 4 XRD patterns of precipitates II prepared with various acids (100 mL) and then heated at 700 ºC, (a) HNO_3, (b) HCl, (c) H_2SO_4, ○; $NdPO_4$.

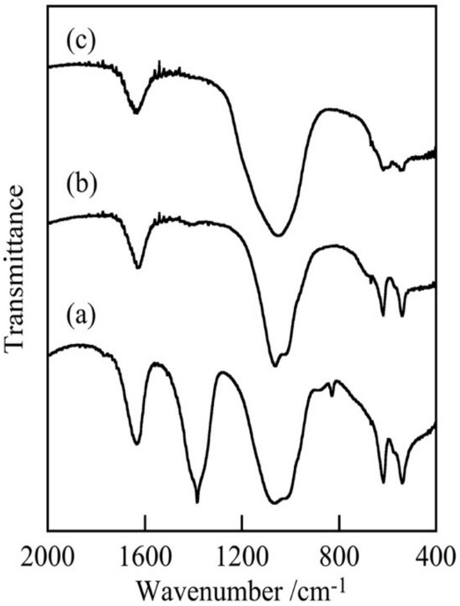

Fig. 5 IR spectra of precipitates II prepared with various acids (100 mL), (a) HNO_3, (b) HCl, (c) H_2SO_4.

(a) (b) (c)

Fig. 6 Photograph of precipitates II prepared with various acids (100 mL), (a) HNO_3, (b) HCl, (c) H_2SO_4.

Precipitate II prepared with nitric acid had absorption peaks at 540, 620, 1,060, 1,385, and 1,635 cm^{-1}, with the peak at 1,385 cm^{-1} due to nitrate ion, 1,635 cm^{-1} due to water, and the others due to phosphoric acid [22]. The precipitate II prepared with sulfuric acid did not have a unique peak because the absorption due to sulfate ions was masked by the absorption due to phosphate ions at 1,050 cm^{-1}. IR results confirmed that all precipitates II contained phosphate.

Neodymium phosphate has a light purple color and appears practically white. On the other hand, iron (III) phosphate can be brown and iron (II) compounds can be green [23]. In this study, it is desired that the precipitate II be white. Fig. 6 shows the photograph of precipitate II prepared with various acids. The precipitate II prepared using nitric acid became white. On the other hand, the precipitate II prepared using hydrochloric acid and sulfuric acid turned brown and dark green, respectively. These showed that the precipitate contained a certain proportion of iron ions.

Table 3 shows Fe/Nd ratio calculated from MP-AES results and recovery ratio in precipitates II. The Fe/Nd ratios were low for nitric and hydrochloric acid and high for sulfuric acid. The Fe/Nd ratio was particularly high for the sample with 100 mL sulfuric acid. The recovery ratios of neodymium were high except when 100 mL of sulfuric acid was used, and higher when 200 mL acids were used. Table 4 shows L^*, a^*, b^* values of precipitate II. The precipitates II prepared using nitric acid showed high L^* value and a^* and b^* values close to zero, corresponding to white color. Precipitates II prepared using hydrochloric acid showed a high a^* value corresponding to redness and a high b^* value corresponding to yellowness. In the precipitate prepared with 100 mL of sulfuric acid, the a^* value was negative, corresponding to green. With 200 mL sulfuric acid, the a^* value was positive and the color of this precipitate II was beige. However, judging by the color of the precipitate, the sample prepared with hydrochloric acid was expected to contain more iron.

Table 3 Fe/Nd ratios calculated from MP-AES results and recovery ratios in precipitate II.

Acid	Conc. (mol/L)	Volume (mL)	Fe/Nd ratio	Recovery ratio Nd	Ratio/% Fe
HNO_3	2.0	100	0.09	49.08	0.61
HCl	2.0	100	0.10	64.51	0.85
H_2SO_4	1.0	100	6.04	17.40	14.81
HNO_3	1.0	200	0.07	69.10	0.70
HCl	1.0	200	0.09	65.52	0.82
H_2SO_4	0.5	200	0.27	111.64	4.23

Table 4 *L, *a**, *b** values of precipitate II.**

Acid	Conc. (mol/L)	Volume (mL)	L^*	a^*	b^*
HNO_3	2.0	100	83.46	3.61	-2.02
HCl	2.0	100	62.00	19.75	35.27
H_2SO_4	1.0	100	73.29	-7.22	7.58
HNO_3	1.0	200	83.89	3.01	-2.89
HCl	1.0	200	63.91	16.78	29.01
H_2SO_4	0.5	200	81.10	4.56	8.50

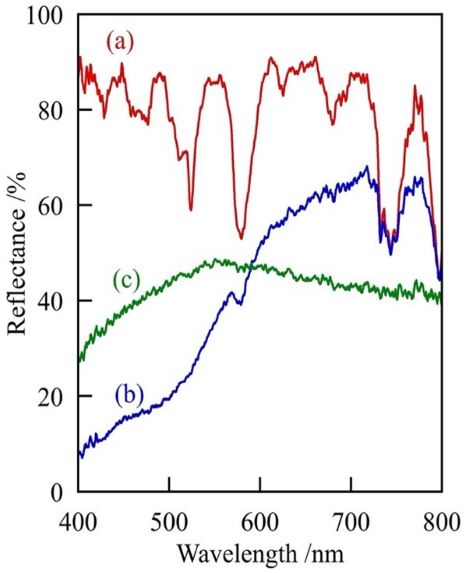

Fig. 7 UV-Vis. reflectance spectra of precipitates II prepared with various acids (100 mL), (a) HNO_3, (b) HCl, (c) H_2SO_4.

The cause of the large difference between the color in Table 4 and the Fe/Nd ratio in Table 3 has not been clarified at this time.

Fig. 7 shows UV-Vis. reflectance spectra of precipitates II prepared with various acids. Precipitate II prepared using nitric acid had the absorption peaks at 430, 476, 524, 580, 625, 680 and 745 nm, which were due to Nd ions [20, 21]. The representative peaks were also confirmed in the spectrum of Precipitate II using hydrochloric acid. On the other hand, no absorption peak due to Nd ions was observed in the precipitate II using sulfuric acid. This was because the neodymium compound was precipitated to some extent in step I, and the amount of neodymium contained in the precipitate II was reduced. These results corresponded to the color of the precipitate.

4. Conclusions

In this study, the waste magnets were dissolved in various acids, pH was adjusted in step I, the generated precipitate was removed, and then neodymium phosphate was precipitated in step II using phosphoric acid and sodium hydroxide. The precipitation of neodymium compound was suppressed in step I by using hydrochloric acid. From the precipitate composition in step II, nitric acid was the most suitable acid for dissolving the waste magnet. Under the condition of sulfuric acid, the precipitate II was dark green and was considered to contain Fe(II) ion.

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