Journal of Alloys and Compounds 408–412 (2006) 1382–1385

Journal of ALLOYS AND COMPOUNDS

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Resource recovery from Nd–Fe–B sintered magnet by hydrothermal treatment

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Available online 28 June 2005

Abstract

The hydrothermal treatment of used Nd–Fe–B sintered permanent magnet was investigated in order to recover the rare-earth resources efficiently. Commercially available Ni-coated $Nd_2Fe_{14}B$ sintered magnet was hydrothermally treated under the optimum conditions at 110 °C for 6 h in the mixed aqueous solution of hydrochloric acid (3.0 mol/dm^3) and oxalic acid (0.2 mol/dm^3). As a result, more than 99% of Nd metal contained in the magnet was collected as solid precipitate of $Nd_2(C_2O_4)_3 \cdot xH_2O$ with the purity as high as 99.8%.

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Keywords: Nd–Fe–B sintered magnet; Nd; Resource; Recovery; Hydrothermal treatment

1. Introduction

Nd–Fe–B permanent magnets with excellent hard magnetic properties are widely applied to various advanced electromagnetic, electromechanical and electronic devices, such as voice coil motors and magnetic resonance imaging. Thus, the amount of industrial production of Nd–Fe–B permanent magnets has been increasing year by year. Consequently, the increment of the disposal amount of used magnets will be anticipated to cause the depletion of their disposal sites, which is one of the serious problems in waste management in Japan. Furthermore, most of the rare-earth resources utilized in Japan are imported from various foreign countries, especially, from China. Japan has always instability to supply rare-earth metals to various industries due to the international change in economical or political affairs. Therefore, recovery method of the rare-earth resources selectively with low cost and high efficiency is desired in order to solve these problems. However, the technique to recover, for example, Nd from various rare-earth magnet scraps, has not been established.

Several recycling processes for the Nd–Fe–B permanent magnet scraps have been proposed in order to solve the depletion problems of natural resources and disposal site. Xu et al. reported a technique to extract only Nd metal from Nd–Fe–B magnet scrap by using molten magnesium metal [1]. Machida et al. described a process to reproduce Nd–Fe–B bonded magnet from the sintered Nd–Fe–B permanent magnet scrap by the melt-spun method [2,3]. However, these techniques have not been practically used as recycle processes for Nd–Fe–B magnet scraps, because the recycled magnets do not exhibit the same property as the permanent magnets prepared from the virginal raw materials. Such difference in quality may be caused by the contamination by impurities in the recycled magnets, which include some oxides or the plated Ni metal used to prevent the oxidation of magnets.

In this study, a selective recovery of Nd metal from Nd–Fe–B permanent sintered magnets was developed by the hydrothermal treatment.

2. Experimental

Commercially available sintered permanent magnet of Ni-plated $Nd_2Fe_{14}B$ was used for experiment. Table 1 shows a typical elemental composition of the magnet. Dysprosium (Dy) is an additive to improve the magnetic properties of the Nd–Fe–B sintered magnet and Ni is plated on the surface of magnet to prevent the Nd–Fe–B sintered magnet

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doi:10.1016/j.jallcom.2005.04.088

Table 1
Typical composition (wt.%) of the magnet

Nd	Fe	B	Dy	Ni	Others
28	68	1	1	1	1

from oxidation. The specimens were sealed together with various kinds of solvents (30 ml) in a pressure vessel lined with fluorocarbon resin. Hydrothermal treatments were carried out by leaving the vessel in a dry oven for 2–24 h at 100–200 °C. In these conditions, pressure in the sealed vessel was estimated to rise up to approximately 1.0–15.6 atm.

After the hydrothermal treatment, specimens were cooled down to room temperature and the precipitates were filtered and collected. The specimens were identified by X-ray diffraction (XRD) using Cu Kα radiation. The microstructural observation and qualitative element analysis of the precipitates were performed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometry (EDS). The thermal behavior of the precipitates was examined by the thermogravimetric and differential thermal analysis (TG-DTA). Purity of precipitate obtained by the treatment was measured by ICP-AES after the complete dissolution in the 6.0 mol/dm^3 of hydrochloric acid.

3. Results and discussion

3.1. Optimum process to recover Nd

The dissolution of not only Nd–Fe–B magnet, but also Ni plated film is required to extract Nd from the magnet. In order to dissolve them, the magnets were hydrothermally treated in various kinds of solvents containing NaOH, H_3PO_4, HCl and H_2SO_4. As a result, strongly acidic solvents were found to suit for dissolution of the magnets. However, these solvents could yield no precipitate of Nd compound, but only the dissolution of magnet occurred. Therefore, some precipitating agents for Nd were required to collect only Nd compound as precipitate. For example, NaCl, ethanol, and $(COOH)_2$ were attempted to use as precipitating agents. After various preliminary experiments, a complete dissolution of sintered magnet and the precipitation of Nd compound were accomplished by the hydrothermal treatment in the following mixed solvents; solution A: HCl and $(COOH)_2$, solution B: H_2SO_4 and NaCl and solution C: H_2SO_4 and ethanol.

As a result of SEM observation, precipitates prepared under all the conditions were found to have the grain sizes of tens of micrometers. EDS analysis of these precipitates showed the constituent elements as follows: (1) Nd, C and O in solution A, (2) Na, Nd, O and S in solution B and (3) Nd, Fe, O and S in solution C. Fig. 1 shows the XRD patterns of precipitates prepared by hydrothermal treatments in the three solvents. It is suggested that these solvents caused the formation of insoluble Nd compounds. However, Fe was contained in the precipitate obtained by hydrothermal treatment in the solution C. The contamination by Fe decreases the purity of the recovered Nd compound. Therefore, it is no use adopting the solution C as solvent for selective collection of Nd compound. XRD patterns in Fig. 1 (a) and (b) showed only the diffraction lines identified as $Nd_2(C_2O_4)_3{\cdot}xH_2O$ and $NaNd(SO_4)_2{\cdot}H_2O$, respectively. This result indicates that the sintered magnet can be completely dissolved, and Nd cations are selectively precipitated as insoluble salts by the hydrothermal treatment.

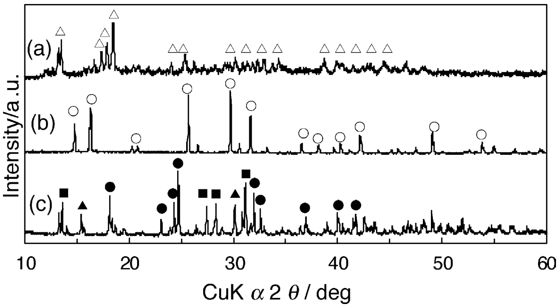

Fig. 1. XRD patterns of the precipitates obtained by the hydrothermal treatment at 110 °C for 12 h with (a) solution A, (b) solution B and (c) solution C. (△) $Nd_2(C_2O_4)_3{\cdot}xH_2O$, (○) $NaNd(SO_4)_2{\cdot}H_2O$, (●) $Fe_{12}O_3(SO_4)_{15}$, (▲) $Nd_2(SO_4)_{3\times 2}{\cdot}H_2O$, (■) $Nd_2H_2(SO_4)_4$.

Generally, Nd_2O_3 is used as a raw material for producing the sintered Nd–Fe–B magnets. Thus, insoluble Nd salts is expected to be oxidized to form Nd_2O_3. It was found by the TG-DTA analysis that $Nd_2(C_2O_4)_3{\cdot}xH_2O$ and $NaNd(SO_4)_2{\cdot}H_2O$ prepared by the present hydrothermal treatment were oxidized at 800 and 1540 °C respectively. The generation of harmful SO_x gas and Na_2O vapor was expected during the oxidation procedure of $NaNd(SO_4)_2{\cdot}H_2O$. Therefore, the best process to recover Nd from the magnets with higher selectivity is the hydrothermal treatment to collect Nd as $Nd_2(C_2O_4)_3{\cdot}xH_2O$ in solution A.

3.2. Optimum hydrothermal conditions

The weight of precipitate obtained by the hydrothermal treatment in the solution A containing 0.25 mol/dm^3 of $(COOH)_2$ at 110 °C for 6 h is plotted in Fig. 2 against the concentration of HCl in the solvent. The weight of precipitate decreased with an increase in the HCl concentration. This behavior will be caused by the redissolution of precipitate with increasing HCl concentration. At the HCl concentrations less than 2 mol/dm^3, the weight of the collected precipitate exceeded the value when all Nd included in the sintered magnet were supposed to be collected as $Nd_2(C_2O_4)_3{\cdot}xH_2O$ (i.e. 310 mg). Fig. 3 shows the XRD pattern of the precipitate obtained at the HCl concentration of 2 mol/dm^3. The diffraction peaks from iron oxalate were identified in addition to those from $Nd_2(C_2O_4)_3{\cdot}xH_2O$. The excess amount of precipitate would be $Fe(COO)_2$ which formed together with the co-sedimentation of $Nd_2(C_2O_4)_3{\cdot}xH_2O$ at low concentration of HCl. As iron oxalate can dissolve in the solvent under only strong acidic

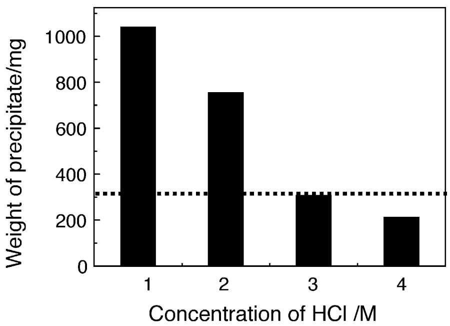

Fig. 2. Dependence of the weight of precipitates obtained by the hydrothermal treatment at 110 °C for 6 h with solution A ([$(COOH)_2$] = 0.25 mol/dm^3) on the concentration of added HCl aqueous solution. Broken line shows the weight of precipitates which was yielded when all Nd contained in the magnet were converted into $Nd_2(C_2O_4)_3{\cdot}xH_2O$.

conditions (HCl > 3 mol/dm^3), the concentration of HCl in the solvent should be kept high enough in order to recover Nd selectively from the sintered magnet. Thus, the optimum concentration of added HCl was 3.0 mol/dm^3 for collecting neodymium oxalate with higher purity by the hydrothermal treatment in the solution A. The optimal concentration of oxalic acid was also investigated. The weight of precipitate increased with an increase in the concentration of oxalic acid. From XRD analysis of the precipitate, the diffraction peaks of iron oxalate were observed at more than 0.3 mol/dm^3 of oxalic acid in the solvent (Figure is not shown). Moreover, the treatment time increased also with an increase in the concentration of oxalic acid at more than 0.3 mol/dm^3. This would be caused by the deposition of neodymium oxalate on the surface of magnet with an increase in the concentration of oxalic acid. It is found, therefore, that the optimal solvent for selective recovery of Nd precipitate from the sintered magnet is the mixture of 3.0 mol/dm^3 of HCl and 0.2 mol/dm^3 of oxalic acid.

Treatment time required for complete dissolution of the sintered magnet depended on treatment temperature. Treatment time required for the complete dissolution of the magnet at 110 °C was 6 h using the optimal solvent. However, the treatment at 100 °C, a glossy thin film fragment, presumably consisting of Ni, was observed after the hydrothermal treatment for 12 h. Therefore, this is attributed to the low dissolution rate of Ni plated on the magnet surface. Thus, more than 110 °C is required to recover Nd selectively from the magnet. Fig. 4 shows the treatment temperature dependence of the weight of precipitate obtained by the hydrothermal treatment in the optimal solvent at the treatment time required for complete dissolution of the sintered magnet. When the treatment temperature exceeds 110 °C at the treatment time of 6 h, the weight of precipitate decreased with an increase in the treatment temperature, and no precipitate was obtained at more than 150 °C. This behavior can be explained by the thermal instability of oxalic acid added as precipitating agent. It is well known under normal pressure that oxalic acid decomposes at more than 180 °C. However, under the present hydrothermal conditions, the pressure within the sealed vessel rises up to about 5.0–6.0 atm. Thus, decrease in precipitated amount in the range from 120 to 140 °C will be due to the increase in solubility of $Nd_2(C_2O_4)_3{\cdot}xH_2O$ into aqueous media cause of partial thermal decomposition of oxalic acid. Therefore, these results should provide the following optimal treatment conditions of treatment temperature and time: at 110 °C for 6 h, respectively.

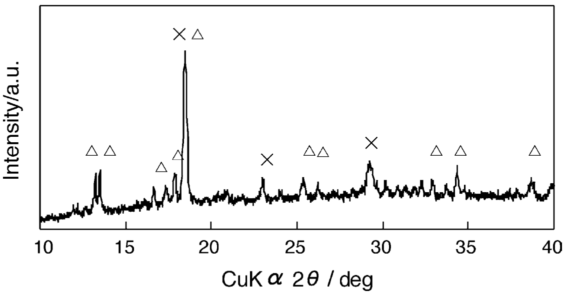

Fig. 3. XRD pattern of the precipitates obtained by the hydrothermal treatment at 110 °C for 6 h with solution A ([$(COOH)_2$] = 0.25 mol/dm^3, [HCl] = 2.0 mol/dm^3). (△) $Nd_2(C_2O_4)_3{\cdot}H_2O$ and (×) $Fe(COO)_2$.

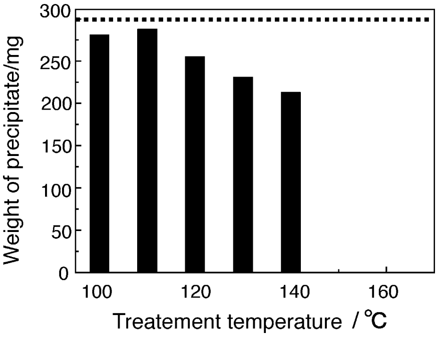

Fig. 4. Treatment temperature dependence of the weight of precipitate obtained by the hydrothermal treatment in the optimal solvent. Broken line indicates the weight of precipitate, which was yielded when all Nd contained in the magnet were converted into $Nd_2(C_2O_4)_3{\cdot}H_2O$.

More than 99% of Nd contained in the magnet was recovered as $Nd_2(C_2O_4)_3{\cdot}xH_2O$ by the hydrothermal treatment in the optimum conditions. This precipitate exhibited so high purity (ca. 99.8%) that the present hydrothermal treatment is effective for selective extraction and collection of Nd as oxalate from the sintered magnet.

3.3. Other element in the wastewater

A large amount of acidic wastewater containing Fe, Ni and B elements will remain after the selective Nd recovery process. Fe and Ni cations dissolved in acidic wastewater can be collected easily as oxalates by their deacidification process. However, there is no effective recovery method for boron species dissolved in aqueous media. The recovery technique of boron in this wastewater will be described in another paper by the present authors.

4. Conclusions

The selective recovery of Nd metal from Ni-coated Nd–Fe–B permanent sintered magnets by the hydrothermal treatment was investigated. The optimal conditions for the hydrothermal treatment were at 110 °C for 6 h in a mixed aqueous solvent of 3.0 mol/dm^3 of HCl and 0.2 mol/dm^3 of $(COOH)_2$. More than 99% of Nd contained in the magnet was collected as $Nd_2(C_2O_4)_3 \cdot xH_2O$. Purity of the recovered $Nd_2(C_2O_4)_3 \cdot xH_2O$ was 99.8%. The present hydrothermal treatment is an effective technique to extract and recover Nd selectively from the sintered magnets.

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