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Purification of rare earth bis(trifluoromethyl-sulfonyl)amide salts by hydrometallurgy and electrodeposition of neodymium metal using potassium bis(trifluoromethyl-sulfonyl)amide melts

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This paper reports a novel bench-scale hydrometallurgical procedure and electrodeposition using potassium bis(trifluoromethyl-sulfonyl)amide (KTFSA) melts for the recovery of rare earth (RE) elements from Nd-Fe-B magnet waste. The investigations were performed at bench scale to assess the potential of a process based on leaching, deironization, and purification of RE amide salts. In the leaching process using 3.4 kg of oxidized Nd-Fe-B and 14.2 L of an aqueous solution of 1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide (HTFSA), 83.0% Nd and 0.98% Fe were leached in 13 h, indicating that selective leaching of RE elements was performed at bench scale. Then, KOH or oxidized Nd-Fe-B was used as a precipitation agent in the deironization process and 100.0% Fe was successfully separated from RE components. Moreover, 4.07 kg of purified amide salts ($M(TFSA)_3$, M = Pr, Nd, Dy, B, Al, and trace elements) were recovered from a spray dryer.

The electrochemical behavior of Nd(III) in KTFSA melts containing $M(TFSA)_3$ (molar fraction of RE components: $x_{RE} = 0.1$) was investigated in this study. Electrochemical analysis revealed that the reduction peak of Nd(III) at around +1.0 V vs. K/K^+ was due to the following reaction: $Nd(III) + 3e^- \rightarrow Nd(0)$. The diffusion coefficient of Nd(III) was estimated to be 3.14×10^{-10} m^2 s^{-1} at 483 K by semi-differential analysis, which is similar to that of Nd(III) in KTFSA melts containing pure $Nd(TFSA)_3$ salts ($x_{Nd} = 0.1$). The electrodeposition of Nd was performed under potentiostatic conditions of +0.8 V vs. K/K^+ at 483 K. The electrodeposits had a fine surface morphology with small metal particles. The electrodeposits were confirmed to be Nd metal in the middle layer analyzed by scanning electron microscopy/energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. Finally, we demonstrated the effectiveness of the novel recovery process for practical use by estimating whole material flow.

1. Introduction

Rare earth (RE) elements are presently regarded to be some of the most critical elements, being essential in future sustainable applications. These elements play a key role in the development of future sustainable technologies, some of which are necessary to achieve a greener global energy profile, e.g., wind power and electric vehicles. Because of their large variety of applications, together with political factors, significant price fluctuations, low availability, and high demand, questions have been raised about their potential recovery from end-of-life products [1]. Urban mining of RE elements has received increased attention over the past decade, with many efforts being directed towards their recovery from products containing permanent magnets.

As one of the effective recovery methods, hydrometallurgy has traditionally been the method of choice for extracting RE elements from primary sources and has shown potential in reclaiming these elements from the aforementioned stream [2]. There have been various techniques for recovering RE elements such as chemical vapor transport [3], solvent extraction [4], electrolysis [5], and electrochemical and hydrometallurgical processes [6,7] (Table 1). The sources of RE elements and remarks on the techniques are listed in Table 1, and it is difficult to maintain high recovery efficiency even at laboratory scale. Despite a number of various recovery studies, large-scale applications to recover RE elements from Nd-Fe-B magnet wastes are not widespread. Little information is available about the few existing plants and their processing paths. This paper reports a large-scale hydrometallurgical procedure to

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Table 1
Various recovery techniques for rare earths.

Methods	Remarks	Reference
Chemical vapor transport	59% Nd and 68% Dy were recovered from scrap of RE intermetallic materials	[3]
Solvent extraction and liquid-membrane transport	The selective permeation of Nd and Dy by IL based supported liquid-membrane using N,N-dioctyldiglycolamic acid	[4]
Electrolysis	Polarization on Pt electrode led to recover Nd and Dy metals in fused Na_2SO_4 from Nd and Dy oxides	[5]
Electrochemical process	Mass ratio between Nd and Dy was indicated as 121 from RE-Ni alloys	[6]
Hydrometallurgical process	The recovery efficiencies were indicated as 69.7% Nd and 51% Dy from magnetic waste sludge	[7]

separate RE components from Nd-Fe-B magnet wastes. The basic research of this hydrometallurgical procedure at laboratory scale has already been reported in previous publications [8,9]. The investigations in this study were performed at bench scale to assess the hydrometallurgical process based on leaching, deironization, and purification of RE bis(trifluoromethyl-sulfonyl)amide salts.

Pyrometallurgical processes using high-temperature molten salts (HTMSs) are well-known conventional methods for the recovery of RE metals. However, the use of HTMSs such as fluorides [10,11] consumes extraordinary amounts of thermal energy owing to the high melting points of molten salts; thus, recovering RE metals from HTMS electrolytic baths is inappropriate. From the standpoint of energy conservation, the development of a recovery process for RE metals with reduced energy consumption is desired. In previous investigations, we demonstrated the recovery of Nd metal using low-temperature molten salts (LTMSs) [12], because an LTMS has many useful physicochemical properties such as a wide electrochemical window, low liquid-phase temperature, and high ionic conductivity. From an environmental point of view, LTMSs are stable compared to organic reagents and prevent the spreading of noxious decomposition chemicals because LTMSs can be recycled back into acid production cycles and be applied repeatedly as an electrolytic bath. Potassium bis(trifluoromethyl-sulfonyl)amide (KTFSA) melts consisting of a potassium cation and a bis(trifluoromethyl-sulfonyl)amide (TFSA) anion, as shown in Fig. 1, are useful candidates for LTMSs. We recently revealed the electrochemical behavior of Nd(III) [12] in KTFSA melts containing dissolved pure $Nd(TFSA)_3$ salts. In this study, we focused on the electrochemical behavior of Nd(III) in KTFSA melts containing dissolved purified $M(TFSA)_3$ salts recovered from Nd-Fe-B magnet wastes via the above hydrometallurgical process. The diffusion coefficient and the kinetic parameters of Nd(III) in this system were also investigated. Based on the fundamental electrochemical analysis, potentiostatic electrodeposition was performed at a relatively large scale. The electrodeposited Nd metal can be applied to the production of Nd-Fe-B magnets because purified Nd metal, except for the oxide layer, was recovered from the electrodeposition using an LTMS bath. Finally, we demonstrated the effectiveness of the recovery process consisting of hydrometallurgy and electrodeposition through the whole material flow.

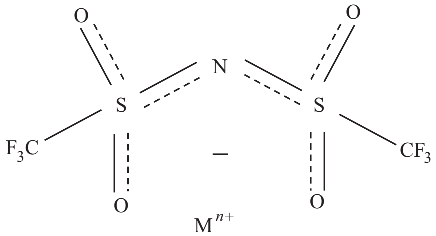

Fig. 1. The structure of metallic bis(trifluoromethyl-sulfonyl)amide; $M(TFSA)_n$, M = Li, Na and K.

2. Experimental

2.1. Pre-treatment process

In this study, voice coil motors (VCMs) were used as a source of Nd-Fe-B magnets for hydrometallurgy and electrodeposition. The Nd-Fe-B magnets were heated in a continuous furnace (S-AP-11.5, DOWA Thermotech Co., Ltd.) to 623 K for 3 h for the demagnetization process to take place. The magnetic flux density before and after demagnetization were measured using a digital TESLA meter (TM-701K, Kanetec Co., Ltd.). It was observed that the residual magnetic force field of the VCM sample was almost zero and the demagnetization percentage was 100.0%. Then, the Ni-Cu-Ni triple thin layer covering the Nd-Fe-B magnet was removed using a grinding machine. After the removal of these layers, fragments of Nd-Fe-B magnets were crushed using a stamp mill (ANS-143, Nitto Kagaku Co., Ltd.) and an automatic mortar (ANM-1000, Nitto Kagaku Co., Ltd.). The resulting fine particles were sieved to <100 μm and heated at $90 K h^{-1}$ to 1133 K, and this temperature was maintained for 3 h in a box furnace (KBF668N1-S, Koyo Thermo Systems Co., Ltd., air flow: $4.0 L min^{-1}$) in order to oxidize the components of the Nd-Fe-B alloy. After the roasting process, these fine particles were ground again using the automatic grinder. The powder properties were investigated using an automatic adsorption apparatus (BELSORP-mini, MicrotracBEL Corp.). The surface area evaluated using the Brunauer-Emmett-Teller (BET) method and the particle size ($D50$) were $0.960 m^2 g^{-1}$ and 15.3 μm, respectively.

2.2. Bench-scale leaching

A schematic illustration of the leaching at bench scale is shown in Fig. 2. The fine powders of oxidized Nd-Fe-B wastes (3.4 kg) after pulverization were introduced into a leaching reactor and leached in 14.2 L of a 1.0 M aqueous solution of 1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide ($HN(SO_2CF_3)_2$, HTFSA). The leaching reactor was heated at 343 K with stirring at 500 rpm. It is important to evaluate the potential (E)-pH diagram of Fe-H_2O and Nd-H_2O systems in the leaching solution to understand the leaching behavior. Therefore, the pH and oxidation-reduction potential (ORP) in the leaching solution were measured using a high-precision digital meter (MM-60R, DKK-TOA Corp.). The measured ORP value vs. a Ag/AgCl reference electrode was compensated for a standard hydrogen electrode. Fe^{2+} was reacted with 1,10-phenanthroline to form an orange-red complex, $[Fe(phen)_3]^{2+}$, and the concentration of Fe^{2+} was measured using an ultraviolet–visible-near-infrared (UV–vis-NIR) spectrometer (Perkin Elmer, Lambda750) with a maximum molar absorptivity at 508 nm [13,14]. The concentration of Fe^{3+} was calculated from the total amount of Fe ions (Fe^{2+} and Fe^{3+}) obtained through inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (ICPE-9000, Shimadzu Co.). All of the accurate concentrations for leaching species were quantitatively determined from ICP-AES analysis.

2.3. Bench-scale deironization and purification of RE amide salts

After the leaching procedure, dried oxygen was bubbled into the leaching solution with a flow rate of $5.0 L min^{-1}$. The oxygen