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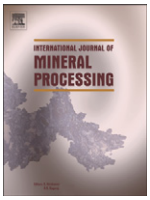

Recovery of rare earth metals from voice coil motors using bis(trifluoromethylsulfonyl)amide melts by wet separation and electrodeposition

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ABSTRACT

In this study, a new recycling process for rare earth metals was developed for voice coil motors (VCMs) from hard disk drives. For the wet separation process, the leaching behavior of finely ground oxidized VCM powder in 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl]methane sulfonamide; $HN(SO_2CF_3)_2$, (HTFSA) aqueous solution was studied. The kinetics of the leaching process for the rare earth metals was explained using the shrinking core model. Then, the selective titration of $Fe(OH)_3$ precipitates was determined from the pH-log[M^{n+}] diagram. The ionic conductivity of the obtained metallic-TFSA melts obeyed the Arrhenius law and the Vogel–Tamman–Fulcher (VTF) parameters were estimated from empirical data. For the electrodeposition process, the reduction behavior of Nd in the metallic-TFSA melts was investigated using cyclic voltammetry, and it was also studied under the potentiostatic condition of −3.2 V at 493 K. The deeper layer of the electrodeposits consisted mainly of Nd metal, which was confirmed by XPS. The oxygen content decreased to less than 0.1% at a depth of 1.0 μm. Thus, the series of recycling processes developed here enabled Fe in VCMs to be selectively removed by wet separation and metallic Nd to be efficiently recovered by electrodeposition.

1. Introduction

In order to avoid unstable supply and prices of resources in Japan, “urban mining,” which consists of extracting resources such as rare earth elements (REEs) from used products, has gained much attention as a new recycling target. From the viewpoint of reducing environmental loading, it is very important to develop economic recycling processes for REEs using “urban mining.” Voice coil motors (VCMs) are an essential component of hard disk drives (HDD) in computers. In fact, their production has been increasing annually, and such parts, after their useful lifetime, are an important “urban mining” target. Thus, it is necessary to develop an economic recycling system and a technology for recovering REEs in order to ensure a stable supply of these resources in our country without being dependent on the social or economic status of any other country.

Pyrometallurgical processes using high-temperature molten salt (HTMS) are well known to the conventional method for the recovery of RE metals. However, the HTMS such as fluorides consumed extraordinary amounts of thermal energy due to high melting points of molten salts, so that it is inappropriate to recover RE metals from HTMS electrolytic bath in Japan. Therefore, from the standpoint of saving energy, it is hopeful to develop the recovery process for RE metals with energy consumption reduction. In previous studies, we have investigated on the recovery of RE metals using low-temperature molten salt (LTMS) and ionic liquid (IL), especially, because LTMS and IL have many well-known useful physicochemical properties such as a wide electrochemical window, a low liquid phase temperature, and relatively high ionic conductivities. Recently, a novel recovery process (Ishii et al., 2012) for VCMs by the electrodeposition of Nd (Kondo et al., 2012a,b) and Dy (Kurachi et al., 2012; Kazama et al., 2013) using low-cost (2 €/kg) ammonium-based and low-viscosious phosphonium-based ILs was demonstrated in our laboratories. Moreover, total consumed thermal and electrodeposition energies using LTMS and IL electrolytic baths would correspond to approximately 1/10 against the conventional methods using HTMS. In this study, we developed the recovery process constituted from multi-stage such as dismantling, demagnetization, chemical etching, oxidizing roasting, acid leaching, synthesis of metallic-bis(trifluoromethyl-sulfonyl)amide; $(N(SO_2CF_3)_2^-$, TFSA salts and electrodeposition using metallic-TFSA melts as shown in Fig. 1. There were no reports about the metallic-TFSA melts as an electrolytic bath in order to recover RE metals. The uniqueness of this technique was that it provided to have an efficiency of RE recovery on the cooperation of both wet separation and electrodeposition processes using LTMS medium. The advantage of this recovery process is that there are almost no secondary wastes because wet separation and the electrodeposition processes are continuously performed and work in close cooperation

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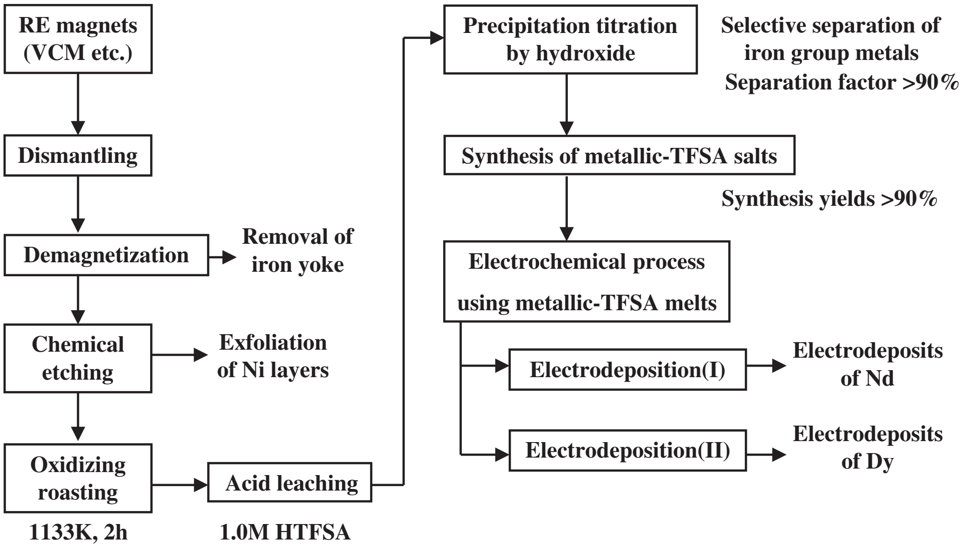

Fig. 1. Novel recovery process of RE metals from VCM by wet separation and electrodeposition.

with one another. Moreover, LTMS medium was composed of the metallic TFSA-based salts (Kubota et al., 2008; 2010) with eutectic composition.

2. Experimental

2.1. Chemical procedure for recycling of Nd–Fe–B magnets

Nd–Fe–B permanent magnets from 3.5-inch hard disk drives (HDDs) were employed as the waste product for the recycling process. The voice coil motor (VCM) in a 3.5 inch-HDD was dismantled and separated from Al metals. Nd–Fe–B magnets were heated to the Curie temperature (583 K) at 90 K/h in an electric muffle furnace. In this demagnetization process, the iron yoke in contact with the VCM was dislocated from the REE-containing magnet. The magnetic flux density of the Nd–Fe–B magnet was measured using a digital TESLA meter (KANETEC Co., Ltd., TM-701) before and after the demagnetizing treatment. The magnetic flux density before and after this treatment was 440 mT and less than 0.1 mT, respectively. Thus, the demagnetization ratio was performed at 99.9%. Then, an alkaline exfoliation solution was prepared by mixing ENSTRIP EN-79B (Meltex Inc.) and sodium hydroxide (Wako Pure Chemical Industries, Ltd., >99.5%) in distilled water. In the chemical etching process, the Nd–Fe–B magnet components of the VCM were immersed in the exfoliation solution at 363 K, after which the Ni coating on the Nd–Fe–B magnet had been selectively dissolved. Generally, this coating is composed of Ni–Cu–Ni triple layers and it is easy to remove the middle Cu layer using a polishing treatment. After the chemical etching process, the Nd–Fe–B magnet was pulverized into small fragments and a fine Nd–Fe–B powder was obtained using an automatic milling treatment. Then, this fine powder, which had a particle diameter of less than 100 μm, was sintered at 1133 K for 2 h in an alumina crucible in an oxidizing roasting process. After the first oxidizing roasting process, grain growth was observed in the sintering powder. Then, a fine powder was obtained again in a second pulverization and a further oxidizing roasting process. It was hoped that the Nd–Fe–B powder was adequately oxidized, as insufficient oxidation leads to the dissolution of excess Fe components in the subsequent dissolution process. In this study, the oxidized Nd–Fe–B powder was immersed in a 1.0 M 1,1,1-trifluoro-N-[(trifluoromethyl) sulfonyl]methane sulfonamide ($HN(SO_2CF_3)_2$, HTFSA, Kanto Kagaku, >99.0%) aqueous solution at 343 K and leaching tests were carried out for leaching times up to 24 h. In order to determine the effect of oxidization, an unoxidized VCM bulk sample was also employed as a leaching test sample. The leaching kinetics experiments were carried out in an HTFSA bath heated in a 250-cm^3 glass flask. The leaching test was conducted at a constant temperature of 343 ± 1.0 K, and the mixture was stirred using a stirring bar driven by a variable speed motor. A total of 250 ml of the 1.0 M HTFSA aqueous solution was put in the reactor and preheated to the desired leaching temperature, and then, 10.0 g of oxidized Nd–Fe–B powder was placed into the reactor and rapidly stirred for various leaching times. After the completion of each experiment, samples were collected using a Pasteur pipette, rapidly transferred to a measuring flask, and diluted 100 times with distilled water and left to cool to room temperature. Then, the centrifuged solution was analyzed for each metallic component by ICP-AES analysis (Shimadzu Co., ICPE-9000).

The selective separation of Fe metal was performed by a precipitation titration process. Various titrants such as alkali-metal hydroxide, alkaline earth-metal hydroxide, and ammonium solution, and their mixtures were investigated. It is important to note that the ionic valence of the Fe species was generally Fe^{2+} in the HTFSA aqueous solution (Matsumiya et al., 2013). This Fe^{2+} ionic species was oxidized to Fe^{3+} by the reaction with concentrated HNO_3 solution for 9 h at 363 K. In this study, the pH-log[M^{n+}] diagram for each metallic species in HTFSA aqueous solution was determined from the precipitation titration of $Fe(OH)_3$. Different titrants such as LiOH, NaOH, and KOH were used for the precipitation titration. The terminus of the titration was confirmed by the formation of $Fe(OH)_3$ precipitates. After the complete elimination of Fe components by centrifugation at 10,000 rpm for 10 min (Model 3740 Kubota Corp.), the HTFSA aqueous solution was evaporated at temperatures up to 423 K. The metallic-TFSA salts obtained in the form of fine powders were dried under vacuum at 393 K for 72 h. The metallic composition of the salts, $M(TFSA)_n$ (M = Pr, Nd, Dy, B, and the trace elements Al, Co, Cu, Ga, and Si), was examined by ICP-AES. The NH_4^+ contents of the metallic-TFSA salts were analyzed by ion chromatography (ICS-1500, Dionex Corp.) The melting temperature of these metallic-TFSA salts was measured by differential scanning calorimetry (DSC6220, Seiko Instruments Inc.).

2.2. Electrochemical procedure for the VCM recycling process

After the above wet separation process was used to remove Fe metal, the electrochemical behavior of the metallic-TFSA melts based on NaTFSA–KTFSA ($x_{Na} = 0.21$) was measured at 493 K by cyclic voltammetry using platinum wire (φ1.0 mm) working and counter electrodes. Platinum wire was also utilized as a quasi-reference electrode because the potential was stable at relatively high temperatures. The