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RECOVERY OF RARE EARTH ELEMENTS FROM NDFEB MAGNET SCRAPS BY PYROMETALLURGICAL PROCESSES

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Abstract

For recovery of rare earth elements from the NdFeB based permanent magnet scraps, a high temperature process was used. Permanent magnets scraps were firstly oxidized in air. The optimal oxidation conditions under air are at temperature of 700°C holding for 30min. After the oxidation process, the oxides were reduced by graphite crucible at 1500°C under Ar atmosphere. By this way, the rare earth elements were recovered in the form of oxides, and Fe was separated to the metal phase. Boron distributed in both the rare earth oxides (REO) containing slag and the metal phase. In order to reduce the boron contents in the rare earth oxides, the carbon saturated iron bath and NdFeB added carbon saturated iron bath were used to refine the slag. By this process, the rare earth oxides with a comparatively high purity of 98.2% were gotten.

Introduction

Rare earth are widely used in green technologies, such as electrical vehicles, novel catalysts, high efficient lighting systems and wind turbines.[1] However, the regional distribution of rare earth ores in the world is uneven. Also caused by the environmental and labors cost of rare earth ore mining, China controls more than 90% supply of rare earth world widely. In 2010, China published the policy to protect the domestic rare earth sources. Because of the increasing demand and supply shortage, additionally triggered by the restriction on the export, the prices of the rare earths have a sharp increase.[2-6]

In order to explore new rare earth resources, plenty of researches have been done on recovery of the rare earth elements, especially from tailings, permanent magnets, waste fluorescent lamps and rechargeable batteries.[3, 7-9] The content of rare earth elements in permanent magnets is more than 30%. During the production of the permanent magnet, including smelting, smashing and grinding, 30%-40% of NdFeB alloys was wasted as useless materials.[10] Because of the oxidation of the NdFeB materials in high service temperature, the life of the magnets is shorten. It is necessary to recover the rare earth elements from the permanent magnet scraps, sludge and the end-of-life magnets.[11-14]

Several methods have been proposed on the recovery of the rare earth elements from the NdFeB magnets. The most traditional methods are based on the hydrometallurgy process, in which the chloric acids, sulfuric acids and oxalic acids will thus be used and introduce some inevitable pollutions to environment. Compared to the hydrometallurgy process, the pyrometallurgical methods are environment friendly. Based on the strong affinity of rare earth elements to oxygen, Nakamoto et al. extracted the rare earth elements as oxides from neodymium magnetic sludge and found that the boron oxides concentration in the slag phase is decreasing with the holding time prolonging in a graphite crucible at 1550°C.[15] The extraction of Nd from waste NdFeB alloys by the glass slag method was also proposed by Saito et al., in which way, boron oxide was used as the extraction agent.[16] Uda used $FeCl_2$ to recover the rare earths from magnet sludge by transforming the rare earth elements into corresponding rare earth chlorides and further separated the rare earth chlorides by vacuum distillation.[17] The metallic alloy methods were also proposed. Takeda et al. used magnesium as extraction medium to extract the rare earth elements by controlling temperature difference inside the reaction vessel. The rare earth elements were separated from the magnet as Mg-Nd alloys, and the rare earth metal was finally gotten by vacuum distillation.[18] The use of silver was also proposed, and the rare earth oxide were gotten as the final production of the process.[19] Some other methods, such as electrolysis method[20] and carbonylation method[21], also provide alternative ways to recover the rare earth elements from the permanent magnet.

In this paper, a pyrometallurgical method was used to recover the rare earth elements from the NdFeB based magnet. The NdFeB materials was firstly oxidized and then reduced in high temperatures, in which process the Fe_2O_3 and part of B_2O_3 were reduced to metal phase by graphite crucible and the rare earth oxides remained in the oxides phase. After separating the oxides and the metal phase, the rare earth oxides are recovered. Novelly, the iron metal and the NdFeB added iron metal bath were used to refine the rare earth containing oxide phase.

Experimental

2.1 Materials

The raw NdFeB materials used in our research are commercial magnet ingots (diameter 9mm × height 12mm) without magnetizing. The elements concentration of the magnets are listed in Table I. The iron used in the experiments for the metal bath is with the purity of 99.99%. The purity of the graphite crucibles are more than 99.99%.

Table I. Composition of the bulk NdFeB magnet (mass %)

Fe	Nd	Pr	La	B	Al
61.60	30.73	4.39	1.58	0.96	0.83

2.2 Experimental process

The process of recovery of the rare earth oxides from the NdFeB materials is displayed in Figure 1(a). Details of the experimental setup in the reduction and refinement processes are shown in Figure 1(b). The electric furnace was heated by $MoSi_2$ heating elements. During the experimental process, Ar (200ml/min) was used as protective gas. The illustrations of the refinement of the rare earth oxides by carbon saturated iron bath or NdFeB added carbon saturated iron bath are given in Figure 1(c).

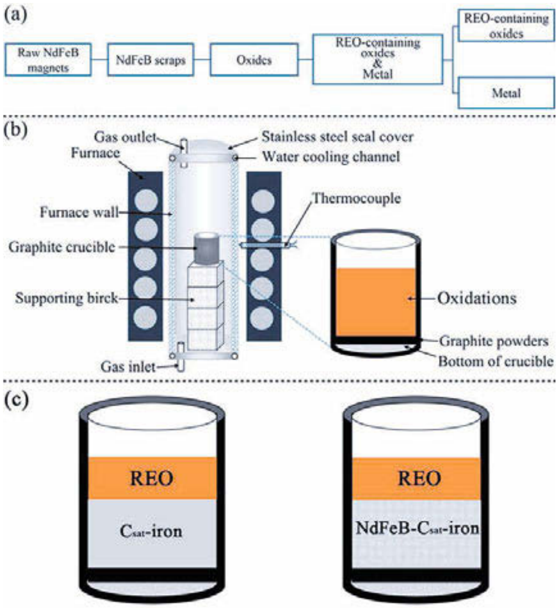

Figure 1. The flowchart of the process of recovering rare earth oxides from permanent magnets (a), the schematic diagram of apparatus used in the reduction and refinement processes (b), and the illustration of the refinement by metal baths.

2.2.1 The oxidation process

Before the reduction process, the rare earth elements should be transformed to corresponding oxides. The oxidation behaviors of the NdFeB materials were investigated by TG-DSC at different temperatures (400, 500, 600, 700, 800 and 900°C).

2.2.2 The reduction process

After the oxidation process, the oxides (REO-Fe_2O_3-B_2O_3) were gotten, and further used in the reduction process. At the reduction temperature of 1500°C, Fe_2O_3 was reduced to iron. The rare earth oxides were still remained in the oxides phase. After this process, the REO containing slag and the iron based metal phase were produced. By separating the slag from the metal, the rare earth oxides was finally gotten.

2.2.3 Refinement of the rare earth oxides

In present experimental temperature, the alumina and boron oxides can hardly be reduced to metal phase efficiently. The carbon saturated iron metal bath and the NdFeB added carbon saturated iron metal bath were used to refine the REO containing slag that gotten in the reduction process.

2.3 Characterization

The particle size of NdFeB powders was measured by particle size analyzer (Mastersizer 2000). The NdFeB samples were tested by differential scanning calorimetry (DSC) and thermogravimetry (TG) with a standby of 20min to stable the facility at 40°C. Then the sample was heated to corresponding temperature with heating rate of 20°C/min in Ar atmosphere, and holding at the experimental temperature for 1 h in Air. The enthalpy curves were normalized to 1 mg, and sapphire was used as reference material to achieve the calibration. Backscattered-electron microscopy (SU-1510, HITACHI) with energy X-ray spectroscopy (Oxford INCA EDS system) was used in characterizing the morphology of the REO-containing slag phase and the elements distribution. The concentration of Nd, Pr, La, Al, Fe and B in both the oxides and metal phase was measured by inductively coupled plasma atomic emission spectrometer (PE400, Perkin Elmer), and the content of Carbon in the metal phase was measured by CS analyzer (CS 600CR, LECO).

Results and discussion

3.1 The oxidation process

In order to accelerate the oxidation process, the NdFeB ingots were pulverized into fine particles mechanically. The particle size was controlled under 150μm. The distribution of the particle size was shown in Figure 2. Obviously, the homogeneous NdFeB samples were gotten. The mean volume diameter is at about 64μm. Then this sample was taken for oxidation experiments using DSC-TG.

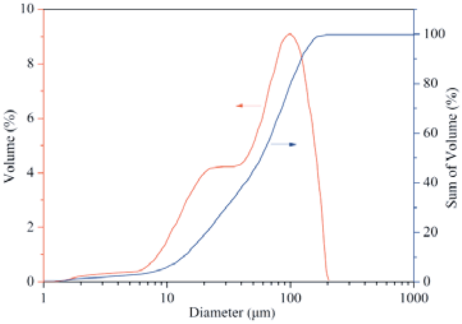

Figure 2. The distribution of particles size of the NdFeB powders.

Figure 3 shows the TG curves of the NdFeB samples under different experimental conditions. Even under the Ar (with purity of 99.999%) atmosphere, the mass increase of the samples is apparently due to the oxidation of NdFeB samples by the residual oxidizing gas (O_2 and H_2O) in Ar. After the oxidation temperature reached, the synthetic air was introduced into the chamber of the TG-DSC facility, and the samples were hold at the oxidation conditions for 1h. Under the air atmosphere, the samples were oxidized intensively with an explosive growth of the sample mass within a few seconds. Then the mass change of the sample slows down in the following holding time. The oxidation process was not finished at temperatures of 400, 500 and 600°C showing by the continuous growing curves in Figure 3. However, the curves of TG at the temperatures of 700, 800 and 900°C present stable tendency after a certain time, which means the oxidation process is basically finished. The oxidation process finished in 35min for experiments both at temperature of 700 and 800°C but in 20min for the experiments at 900°C. The total mass change of the sample at 700, 800 and 900°C are all at about 31% which match well with the calculated value from the composition from Table 1. It confirmed that the NdFeB material can be fully oxidized under 700, 800 and 900°C in a short time arranging from 20 to 35min.

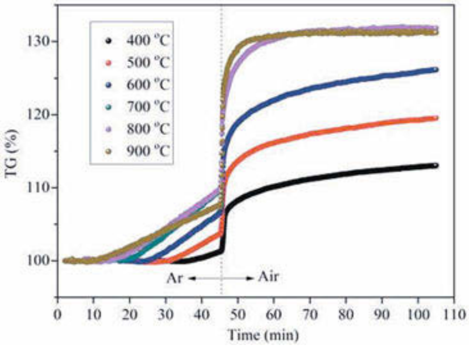

Figure 3. The TG curves of the NdFeB samples heated at different temperatures.

The oxidation process is an intensively exothermic process, as shown in Figure 4(a). The heating program is shown in Figure 4(b). After reaching the isothermal stage, the oxidation process was start under air. The exothermic peaks was shown in each of the DSC curves. Although the ΔH of the oxidation will decrease with increasing of temperature, the main exothermic peak becomes sharper as shown in Figure 4(a). It indicated that the oxidation rate increases with the increasing of experimental temperature. The arrows in Figure 4(a) show small exothermic peaks appears in each of the DSC curves except the one at 400°C. Edgley et al. had reported that the oxidation of NdFeB magnet was a transgranularly oxidation process.[22] Higher reaction temperature improves the reaction rate and accelerate the decomposition of the main $Nd_2Fe_{14}B$ phase. A new surface of the samples will be further oxidized relevant to the second oxidation exothermic peaks.

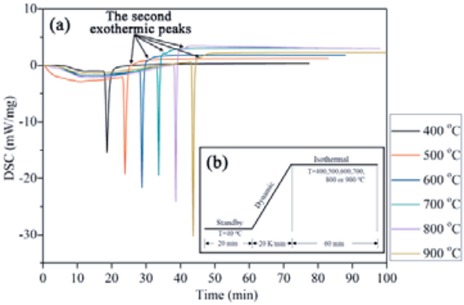

Figure 4. The DSC curves of NdFeB samples in different conditions (a), and the heating program (b)

To ensure the rare earth elements were fully oxidized, the temperature of 700°C and the holding time of 30min are considered as the optimal oxidation conditions. After the oxidation process, higher temperature will lead to further sintering process or formation of $NdFeO_3$.[23]

3.2 The separation of REO and metal phase

After the oxidation process, REO, iron oxides, alumina and boron oxides were produced. Figure 5 shows the standard Gibbs energy for each elements in the raw magnet also with Carbon. The thermodynamic calculations were performed using HSC chemistry 5.1 software for windows.[24] The rare earth elements Nd, Pr and La have very similar thermodynamic properties, so only the oxygen potential of Nd is shown. Thermodynamically, Fe_2O_3 can be reduced to iron easily by carbon around 700°C. B_2O_3 will be reduced by carbon at temperatures over 1650°C. The other oxides, such as alumina and rare earth oxides, are hardly reduced by carbon under the experimental temperatures. Based on the difference of the thermodynamic properties, Fe_2O_3 can be reduced into metal phase and the rare earth elements were remained in oxide phase by controlling the temperature of reduction process.

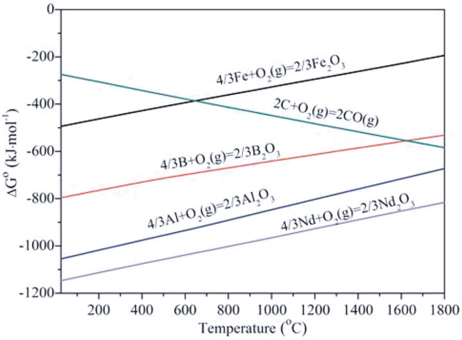

Figure 5. The chemical equilibrium of the elements in the NdFeB materials with oxygen.

The products of the reduction process is shown in Figure 6(a). It displays the slag phase and the metal phase separated clearly. The initial content of the oxides in the crucible was labeled by the white dash line. Different from the traditional metallurgical process, the slag has not flowed up to the top of the metal phase. The density of the REO-containing oxides is similar to the metal phase, which resulting in the slag and the metal phase separated left and right. The temperature of reduction process was program controlled as shown in Figure 6(b). Holding at 1200°C for 2h is mainly for the reduction of iron oxide in solid phase. And the holding time of 4h at 1500°C is for the reduction of boron oxide and separation of the slag and metal. During the reduction process, CO released due to the reaction of Fe_2O_3 and graphite crucible. The emission of gas from solid phase is easy. However, if the reduction happened at 1500°C, the oxides will melt and the release of the gas become hard. And the splash of the melts will happen.

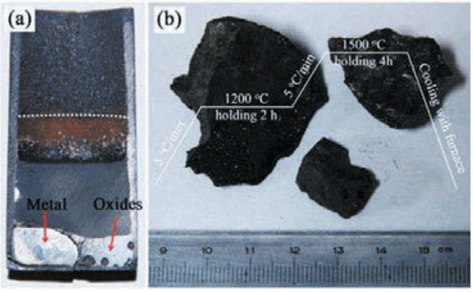

Figure 6. The productions of the reduction process (a), and the rare earth oxides separated from the metal phase also with the reduction heating program (b).

After reduction process, the REO containing oxides phase and the iron based metal phase are separated. By this process, the rare earth oxides were produced, as shown in Figure 6(b). From the BSEM image of the oxide phase, shown in Figure 7, different phases are observed. Fe in the slag phase is the iron droplets that remained in the slag. Aluminum distribution in the oxide phase is because of the $REAlO_3$ peroskite phase.[25]

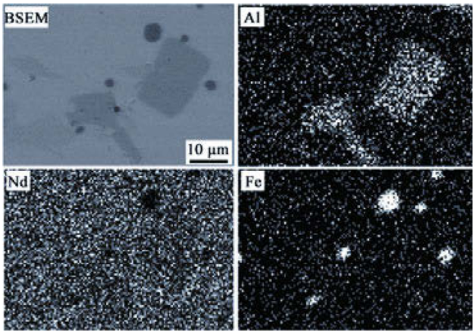

Figure 7. The BSEM of the rare earth containing slag also with the EDS mappings of Al, Nd, and Fe.

3.3 Refinement of the REO containing oxides

The concentration of the oxides and the metal was listed in Table II. At the experimental temperature, Fe_2O_3 can hardly exists in the oxides phase. The concentration of the oxide phase was normalized without considering the appearance of Fe. Normally, the content of Fe measured by ICP is about 0.2% in all slag samples. The concentration of the oxide phase and the metal phase confirms that the rare earth oxides are concentrated in the slag phase and the iron oxides are reduced to the metal phase by the reduction process.

After the reduction process, boron oxides content in the oxide phase is 4.59%. Referring to the calculated results from Figure 4, the carbothermic reduction of B_2O_3 is at about 1650°C. However, some researchers have investigated the production of boron carbides. The reaction becomes thermodynamically feasible above 1400°C.[26] After the reduction process of 4h at 1500°C, the content of B in the metal phase is 0.06%.

Table II. The concentrations of the oxide phase and the metal phase

Exp. No.	Oxide Phase (mass %)					Metal Phase (mass %)					
	Nd_2O_3	Pr_2O_3	La_2O_3	Al_2O_3	B_2O_3	Nd	Pr	La	Al	B	C
1	77.38	11.28	5.35	1.39	4.59	0.08	0.01	<0.01	0.03	0.06	3.45
2	78.55	11.10	5.29	1.36	3.70	0.04	0.01	<0.01	0.02	0.13	3.78
3	80.26	11.53	5.49	1.57	1.15	0.02	<0.01	<0.01	0.01	0.45	2.56
*No.1 Reduction process; No.2 Refining by C_{sat}-iron bath; No.3 Refining by NdFeB added iron bath											

For the refinement of the REO containing oxides, the oxides gotten from the reduction process with concentration listed in Table 2 were used in the refinement process. After the refinement by C_{sat}-iron bath, the concentration of the boron oxides in the oxides phase shows a slight decrease, and the content of B in the metal phase is 0.13%. It confirms that the reduction of B_2O_3 by carbon at 1500°C is available. In the refinement process of holding for 4h at 1500°C, 20g rare earth containing slag and 60g pre-melted iron bath were used. Because of the mass ratio of slag and metal decrease, the interface of the slag and metal increase. It helps the reduction of B_2O_3.

Considering the carbon thermal reduction of B_2O_3 is not efficient, the raw NdFeB materials were added to the C_{sat}-iron bath. After this refinement process, the content of B_2O_3 in the oxides phase decrease dramatically, and the content of boron in the metal phase increase apparently. By this method, the purity of the rare earth oxides reached 98.2%. The purities of the rare earth oxides by the reduction process and by the refinement using C_{sat}-iron metal are 94.0 and 94.9%, respectively.

Conclusion

In order to recover the rare earth elements from permanent magnet, the NdFeB materials were oxidized under Air. Following by a high temperature reduction process, the rare earth oxides and the iron based metal phase separated successfully. For high purity of the rare earth oxides, the refinement by C_{sat}-iron bath and NdFeB added C_{sat}-iron bath were used.

High temperature helps in the oxidation process of the NdFeB materials both in the oxidation rate and the decomposition of the magnet. While the oxidation process is an energy consuming process. The experimental temperature of 700°C and holding time of 30min were the optimal conditions for oxidation.

By the reduction process, the rare earth oxides with a purity of 94% were gotten. After the refinement by C_{sat}-iron bath, the impurity of the rare earth oxides improves slightly to 94.9%. However, the impurity of the oxides reached 98.2% by using the refinement of NdFeB added C_{sat}-iron bath. Hence, a new method to obtain rare earth oxides from permanent magnet was achieved. This method is feasible both to the magnet scraps and sludge.

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