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RECOVERY OF RARE EARTH ELEMENTS FROM EOL PERMANENT MAGNETS WITH SLAG EXTRACTION

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Abstract

High temperature molten slag extraction of rare earth elements (REEs) from End-of-Life (EoL) permanent magnets in Hard Disk Drives (HDDs) was experimentally investigated. The HDDs were shredded, and after thermal demagnetisation, crushing and screening, NdFeB enriched scrap was obtained for the experiments. Two slag systems of $CaO\text{-}SiO_2\text{-}Al_2O_3$ and $CaO\text{-}CaF_2$ were tested with more than 99% recovery of REEs. The REE-rich slag will be used for hydrometallurgical extraction and the separated iron-rich alloy can be a good source of raw materials for steelmaking. The advantages of molten slag extraction is its capability of effective separation of REEs and iron, and the recovery of both fractions at the same time.

Introduction

Neodymium-iron-boron ($Nd_2Fe_{14}B$) permanent magnets have revolutionised the production of small lightweight electronic equipment that is powered by small motors. They are nowadays found in a wide range of consumer electronic products that have become indispensable in our modern lifestyle. One of the major applications of $Nd_2Fe_{14}B$ permanent magnets is the computer hard disk drives (HDDs) which is accountable for, about 31% of the application market[1]. A typical HDD has magnets in two locations: at the spindle motor in the centre of the disk; and at the voice coil motor. It contains a few tens grams of $Nd_2Fe_{14}B$. A predicted shortage of rare earth elements (REEs) has been recently reported, driven by the growing demand in high-tech sectors. There are concerns in stable and sustainable market supply of these strategic raw materials from primary resources. On the other hand, the secondary resources from various kinds of waste streams are readily available but not efficiently utilised or recycled, and are receiving more and more attentions.

From technological aspects, there are many possibilities for REEs recovery, including the hydrogen decrepitation[2], chemical vapour transport[3], liquid metal extraction[4] and hydro- and pyro- metallurgical processing[5-7]. The complex composition of the HDDs causes excessive contamination during their shredding. This introduces great new challenges which will be explored in the experimental part of this study. The present paper introduces the experimental results on molten slag extraction of REEs from EoL shredded HDDs. The objective of the present study is to develop a feasible route for the recovery of rare earths from $Nd_2Fe_{14}B$ magnets in HDDs in the end of life (EoL) products, therefore, closing the life cycle of the REEs' application. Slag extraction is the first step to separate REEs from the steel and aluminium based bulk metal compositions. The REE will get enriched in the slag phase and will be extracted with hydro- or pyrometallurgical reduction processes.

Experimental

Raw materials

Two types of REE-bearing materials from HDD shredder received from Van Gansewinkel Group (VGG) were used in the experiments. The coarse and fine (< 1 mm) fractions from the shredded HDDs. The fine fraction was produced by physical processing of the coarse scrap after demagnetising, size reduction and screening. The fine fraction contains, on average, 42% Fe, 14.2% Nd, 9.6% Ni, 5.1% Al, 2.3% Si, 1.6% Pr, 1.5% Cu, 1.3% Zn, 0.9% Co, 0.8% Tb and other minor or trace elements. The coarse scrap contains additional metallic pieces (mostly steel) that, due to their large size, could not be accurately quantified. Boron was not examined in the present study due to the limit in the X-Ray analysis. The reagent grade oxides CaO, SiO_2, Al_2O_3 and CaF_2 were used for preparation of extracting slag.

Equilibrium experiments

A chamber furnace was used for the smelting tests to extract the rare earth in the scrap into molten slag. The scrap and the oxide mixture with designed compositions are charged into a working crucible with controlled ratio. The sample was heated to 1500°C for smelting, and equilibrated at 1500°C for 3 hours under inert atmosphere. After the equilibrium, the sample was cooled to 700°C at a rate of approximately 10°C per minute, and then the furnace was switched off for natural cooling. The crucible was taken out of the furnace at the room temperature, and the slag and metal were separated for further analysis with XRF/XRD and SEM/EDS/EMPA.

Results and discussion

The selective molten slag extraction is based on the higher affinity of the rare earths to oxygen than iron and other metals in the scrap. Three major parameters were examined including the slag composition, slag to metal (S/M) ratio, and scrap type. Table 1 lists the experimental conditions and results.

Two slag systems were chosen: a slag consisting of 40 CaO-40 SiO_2-20 Al_2O_3 (in wt%) with melting temperature about 1300°C and a low melting fluorspar slag with 35CaO-65CaF_2 (in wt%). The latter slag system was used by Müller & Friedrich[7] for REE extraction from

NiMH rechargeable battery. Thermodynamically CaO and CaF_2 are more stable than RE-oxides and RE-fluorides respectively under the experimental conditions. Al_2O_3 and SiO_2 in the slag could be reduced by metallic REEs. The REE oxidation could also take place in the presence of small amount of air in the atmosphere. Under the experimental conditions, it is expected that only the REEs will be oxidised into the slag, and oxidation of iron by any of the slag components is less favourable, thus promoting separation between metallic iron and slag. Any oxidised iron that might be present is expected to be reduced either by Nd, Al, or Si in the molten metal phase.

Table 1: Experimental conditions and results

Test no.	Slag system	Smelting conditions	Slag composition, wt%							Metal composition, wt%						
			Ca	Si	Al	Fe	Nd	Pr	Tb	Fe	Ni	Co	Si	Cr	Mn	Nd
1	40% CaO-40% SiO_2 – 20% Al_2O_3	Slag/Scrap: 0.2 Scrap: fine Crucible: Alumina	19.8	10.2	17.0	5.38	34.0	4.39	0.21	93.0	2.40	1.10	1.10	1.00	0.34	0.04
2	40% CaO-40% SiO_2 – 20% Al_2O_3	Slag/Scrap: 0.4 Scrap: coarse Crucible: Graphite	21.5	11.6	9.62	0.58	25.3	4.36	0.13	92.6	1.82	1.40	1.58	0.98	0.38	---
3	35% CaO-65%CaF_2	Slag/Scrap: 0.4 Scrap: coarse Crucible: Graphite	51.1	0.73	0.48	0.54	23.6	3.10	0.14	94.5	1.86	1.07	0.19	0.74	0.30	---
4	35% CaO-65%CaF_2	Slag/Scrap: 0.2 Scrap: fine Crucible: Graphite	27.6	1.49	1.60	4.06	35.5	4.06	0.25	89.7	3.38	0.81	0.25	0.47	0.40	0.04

Most of the tests were conducted by using graphite crucibles. Alumina crucibles were also used for some trials. From the results, it is clear that the coarse scrap and a higher slag to scrap ratio lead to better metal separation of neodymium and iron, with about 0.6 wt% of Fe in the slag. In general, the slag phase is highly enriched with REs (Nd, Pr and Tb), in a range of 25 - 40 wt%. For the smelting of fine scrap, there are certain metallic beads entrapped into slag. XRD analysis of the slag from the CaO- SiO_2-Al_2O_3 slag indicates a complex formation of rare earth compounds during the smelting. Most of neodymium forms complex silicate compound of $Ca_{1.1}Nd_{3.9}(SiO_4)_3O_{0.95}$, and with small amount of Nd dissolving into Ghelenite compound of $(Ca_{1.98}Nd_{0.02})Al(Al_{1.02}Si_{0.98}O_7)$.

The slag system of CaO-CaF_2 gives better coalescence of the metal phase due to a higher metal/slag interfacial tension. Usually a higher iron content in the charged scrap (i.e. the coarse scrap) results in a better separation between the two phases, as well as between rare earths and iron. According to XRD measurements, the main compounds in the slag are CaO, CaF_2 and Nd_2O_3. This is also confirmed by local chemical analysis with EPMA, as seen in Figure 1. Three major phases were identified: RE- phase (bright white), RE-enriched phase (light grey), and Ca-O-F based matrix that contains some trace amount of REs. Nd (and typically some Pr) was detected in all phases except the metallic inclusions in the slag, which suggests that multiple Nd-containing compounds are formed during the smelting, though they are not reflected with XRD patterns. The analysis also confirms that NdF_3 will not form under the smelting conditions, which is in agreement with the thermodynamic analysis.

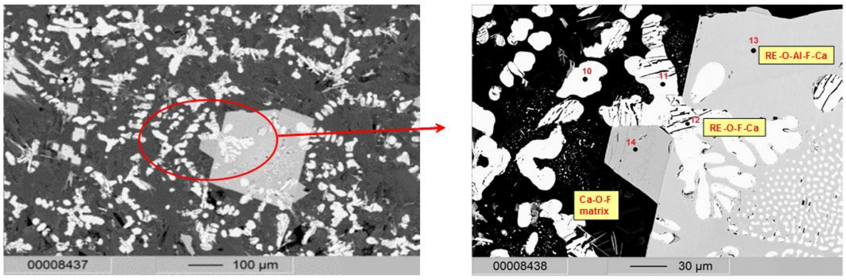

Figure 1: Microstructure of REE-containing slags in CaO-CaF_2 system

Conclusions

Pyrometallurgical slag extraction showed that both slag systems are suitable for almost 100% extraction of REEs into the slag, yielding two products: a concentrated RE-containing slag and an iron ingot. Iron recovery in the metal phase is 99% for the coarse scrap and 95-96% for fine scrap. Keeping a proper slag/metal ratio is necessary for a good metal separation. The REE-rich slag is subjected to acid leaching and REE recovery as fluorides and/or oxides. The iron-based alloy is a good source of steelmaking scrap.

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