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EFFECT OF MAGNET SCRAP SIZE ON THE EXTRACTION BEHAVIOR OF HEAVY RARE EARTH ELEMENTS BY LIQUID METAL EXTRACTION

Liquid metal extraction (LME) process results in 100% neodymium (Nd) extraction but the highest extraction efficiency reported for Dysprosium (Dy) so far is 74%. Oxidation of Dy is the major limiting factor for incomplete Dy extraction. In order to enhance the extraction efficiency and to further investigate the limiting factors for incomplete extraction, experiments were carried out on six different particle sizes of under 200 µm, 200-300 µm, 300-700 µm, 700-1000 µm, 1000-2000 µm and over 2000 µm at 900°C with magnesium-to-magnet scrap ratio of 15:1 for 6, 24 and 48 hours, respectively. This research identified Dy_2Fe_{17} in addition to Dy_2O_3 phase to be responsible for incomplete extraction. The relationship between Dy_2Fe_{17} and Dy_2O_3 phase was investigated, and the overall extraction efficiency of Dy was enhanced to 97%.

Keywords: Liquid metal extraction, Rare earth elements, Recycling, Oxidation, Magnet scrap

1. Introduction

Neodymium (Nd) based permanent magnets store the highest magnetic energy per unit volume as compared to other magnets [1]. Dysprosium (Dy), a heavy rare earth element (HREE) and a critical material [2], is added to enhance the temperature stability of the magnet for improving its ability to perform at elevated temperatures in Nd based permanent magnets [3]. Besides being key component of renewable energy technologies such as wind turbines, Rare earth (RE) magnets are used in Eco-friendly vehicles, electronic devices, alloy elements etc. [4]. With the world's shift towards greener economy, the demand of REEs have tremendously increased but the skewed dynamics of the RE market poses supply-demand risk which need to be urgently addressed.

Substantial researches focused on the recycling of Nd and Dy from permanent magnets using environmentally friendly techniques such as direct melting, electro-slag refining, glass slag method and liquid metal extraction (LME) have been carried out in the past. Process parameters such as calculations of diffusion coefficients, sequences of extraction mechanisms and factors for optimization of extraction process were reported in these studies [5-8]. However, effect of scrap size on the extraction ratio and diffusion behavior have not been studied in detail. A similar study on effect of scrap size from Nd-Fe-B magnet, which did not consider Dy, reported the maximum extraction for Nd to be 96.5% [9]. From other studies, the highest extraction efficiency reported for Dy in LME process so far is of 74% [8].

REs available for recycling are present in different shapes and sizes, therefore, for practical implications six different scrap sizes of different shapes were selected for experimental purposes to gauge the effect of scrap size on the extraction efficiency by the LME process with Mg as an extraction agent. Moreover, the effect of oxidation and the phase transformations during the process were also investigated.

2. Experimental

RE magnets containing ~30wt.% RE were obtained from JAHWA electronic Co. Ltd. for experimental purposes. The stoichiometric composition of these rare earth magnets as analyzed by XRF is shown in Table 1.

These magnets were pulverized using jaw crusher into six different particle sizes of under 200 µm, 200-300 µm, 300-700 µm, 700-1000 µm, 1000-2000 µm and over 2000 µm.

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TABLE 1

Stoichiometric composition of RE magnet

Elements	Nd	Dy	Fe	Minor
Rare earth magnet (wt.%)	25.8	3.5	68.98	1.72

Oxygen content of each sample was measured by Nitrogen-Oxygen-Hydrogen (NOH) analyzer.

Magnesium of 99% purity was procured from JC company. Magnesium was selected as an extracting agent because it selectively reacts with Nd and Dy in the magnet and it hardly forms any intermetallic compound with Fe [5]. Magnesium was grinded to remove the oxidation layer and to fit inside the 1 cm × 1 cm × 10 cm Fe crucible. The LME reactions were carried out in an induction furnace for reaction times of 6h, 24 h and 48 hours at a fixed temperature of 900°C with Mg: Magnet ratio of 15:1. Vacuum was achieved inside the induction furnace up to a level of 1×10^{-2} torr before high purity Ar gas was introduced in the chamber for creating an inert environment in order to prevent oxidation. The heating rate was kept under 10°C/min and the sample was let to cool naturally after the completion of reaction time.

The crucible was cut by diamond blade for observing the cross-section of the (Nd,Dy)FeB-Mg coupled sample. The extraction efficiency was calculated using XRF while the morphology of the cross-section was observed by FE-SEM, and the phases were identified by XRD.

3. Results and discussion

The results of oxygen content of each scrap size are shown in Table 2.

Higher oxidation concentration was reported in smaller scrap sizes which can be associated to the increase in the surface to volume ratio in smaller particle sizes. RE oxidation takes place easily, especially during the grinding process in which the magnet is exposed to atmosphere at a high thermal energy state. As per the microstructural analysis of the cross-sectioned RE magnet scrap-Mg sample after the reaction, the sample can be divided into three zones i.e. unaffected magnet zone, reaction zone and Mg zone. The region where REs had diffused out of the magnet into Mg to form intermetallic compounds was labelled as reaction zone, hence it is the zone of most importance from scientific point of view.

TABLE 2

The oxygen content in RE magnet scrap

Powder size	Under 200 µm	200-300 µm	300-710 µm	710-1000 µm	1000-2000 µm	Over 2000 µm
Oxygen (wt.%)	0.2612	0.2540	0.1773	0.1720	0.1621	0.1134

In order to observe how the scrap size and oxidation content influenced the phase morphology and extraction behavior, the BSE images of the reaction zone of the six different scrap sizes at 48 hours are shown in Fig. 1.

Mg infiltrated the magnet forming black ligaments, and it can be observed from the size of the ligaments in the images that Mg infiltrated more in smaller scrap sizes because of the larger reaction surface. A grey zone (Fe) was formed as a result of the reaction between $RE_2Fe_{14}B$ and Mg. Moreover, nano size particles were observed in all scrap sizes. As shown in Fig. 1(a) and (f) these particles were divided into two categories, (#1) and (#2), depending on their location. Nano size particles in the ligaments were termed as (#1) and nano size particles in Fe-rich area as (#2). The amount of nano size particle (#1) decrease as the size of the scrap increases, whereas, nano-size white particles (#2) increase with the increase in scrap size.

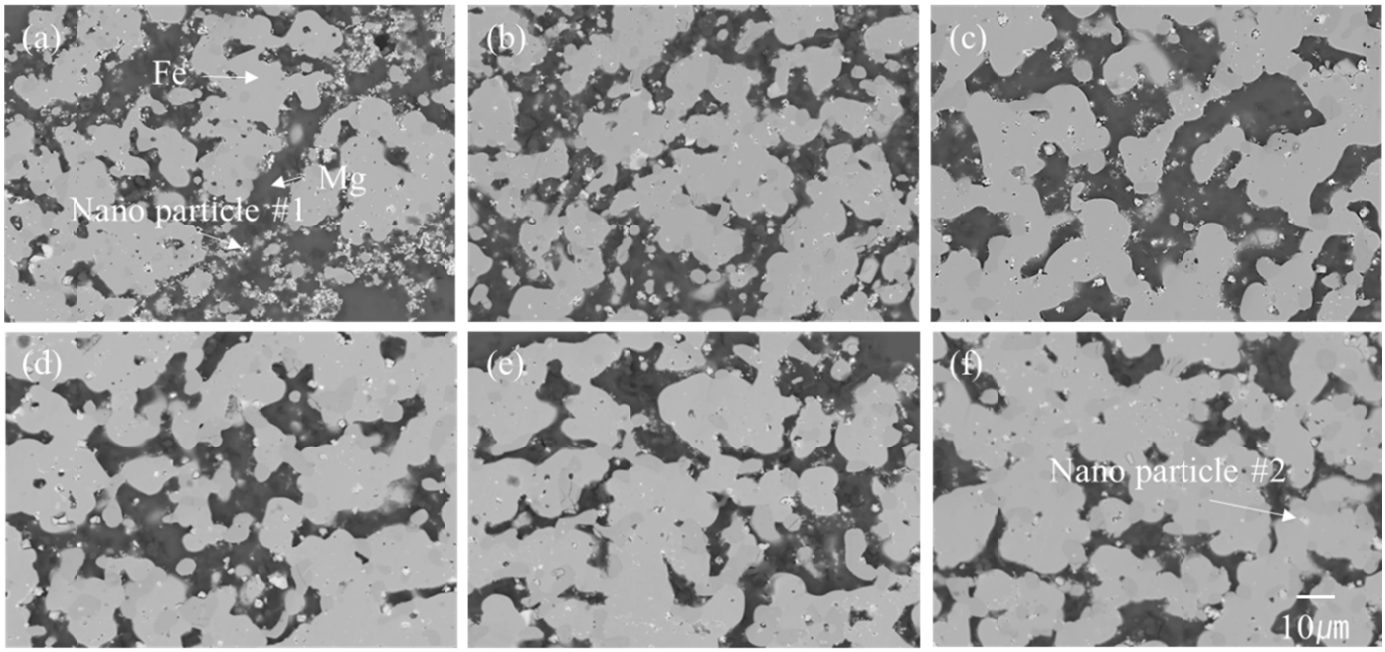

Fig. 1. BSE images of the reaction zone in magnet after 48 hours at 900°C (a) under 200 µm, (b) 200-300 µm, (c) 300-700 µm, (d) 700-1000 µm, (e) 1000-2000 µm, and (f) over 2000 µm

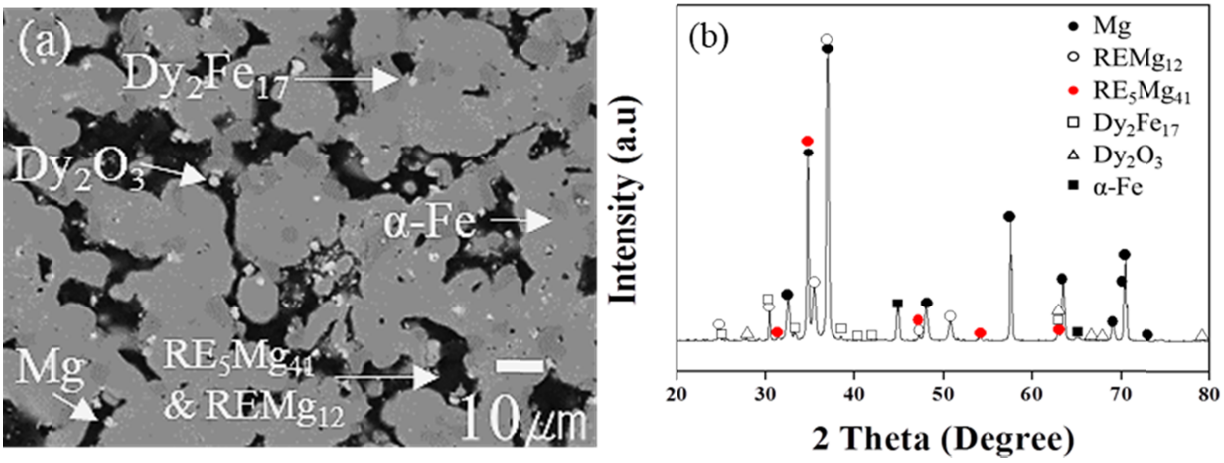

Fig. 2. Microstructure of reaction zone in magnet under 200 μm after 48 hours (a) BSE image, (b) XRD results

The phases identified in the reaction zone are highlighted in Fig. 2(a) from the XRD results shown in Fig. 2(b). As reaction proceeds, the $RE_2Fe_{14}B$, RE-rich phase and RE-oxide in magnet transform into Fe, $REMg_{12}$, RE_5Mg_{41}, Dy_2Fe_{17} and Dy_2O_3 phase in the reaction zone. Nano size particles (#1) were identified as Dy_2O_3 and nano-size particles (#2) as Dy_2Fe_{17} by SEM-EDS and XRD.

The infiltration of Mg and the increase in oxygen content can be directly linked with the extraction efficiency. For observing this linkage, the extraction efficiencies of the six different particle sizes after a reaction time of 6, 12 and 48 hours are shown in Fig. 3.

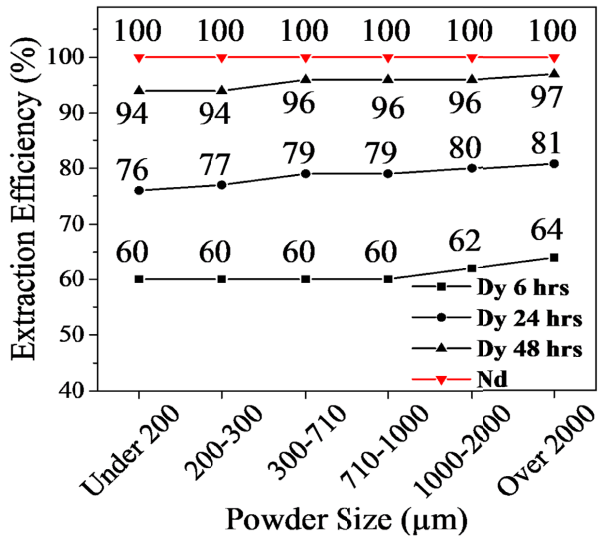

Fig. 3. Extraction efficiency by variation of scrap size with reaction time

As can be seen from Fig. 3 that 100% Nd extraction was achieved irrespective of the particle size and on all reaction times above 6 hours. However, in case of Dy, the reaction time had a significant effect on the extraction efficiency as it increased in all the particle sizes with an increase in reaction time. The overall maximum efficiency of 64, 81 and 97% against 6, 24 and 48 hours, respectively, was achieved in the particle size of over 2000 μm.

Incomplete decomposition of Dy_2Fe_{17} and incomplete reduction of Dy_2O_3 were identified as the reasons for Dy extraction efficiencies of less than 100%. Incomplete reduction of Dy oxide has also been reported by a previous research [8], hence, solution to remove Dy_2Fe_{17} and Dy_2O_3 is needed for complete Dy extraction. The reason for formation of Dy_2Fe_{17} can be explained by the negative heat of mixing value of Dy and Fe, which means that Dy has a stronger affinity for Fe as compared to Nd during reaction [10], whereas, Dy_2O_3 forms due to the presence of oxygen content in magnet.

Moreover, a correlation between the oxidation content of each particle size and respective extraction efficiency was observed. The higher the oxidation of Dy into Dy_2O_3, the lesser was the extraction. For confirming the effect of Dy phase transformation on extraction efficiency, the Dy related phase fractions in each particle size at 6, 24 and 48 hours were measured, and the results are displayed in Table 3.

TABLE 3

Changes of Dy related phase fraction with powder size and reaction time

Time / Powder size	Dy_2O_3 phase fraction (%)			Dy_2Fe_{17} phase fraction (%)		
	6 hours	24 hours	48 hours	6 hours	24 hours	48 hours
Under 200 μm	1.58	0.95	0.28	1.35	0.81	0.09
200-300 μm	1.49	0.88	0.27	1.54	0.85	0.09
300-710 μm	1.30	0.68	0.17	2.30	1.20	0.12
710-1000 μm	1.26	0.66	0.16	2.44	1.27	0.12
1000-2000 μm	1.15	0.60	0.16	2.51	1.32	0.13
Over 2000 μm	0.91	0.48	0.11	2.98	1.57	0.14

The results show a trend of decreasing phase fraction of Dy_2O_3 with increasing particle size whereas it is the opposite for Dy_2Fe_{17} in all the three experimental times. This implies that in particles with lesser oxygen content Dysprosium preferentially reacted with Iron as compared to Oxygen.

This change in Dy-phase fractions across the particle sizes effects the extraction efficiency of Dy i.e. greater the decrease in Dy_2O_3 phase, higher is the Dy extraction efficiency. It can be seen that the extraction rate is highest in the biggest particle size for all three timings. More importantly, the percentage of Dy_2Fe_{17} phase is larger compared to Dy_2O_3 phase in all the particle sizes but percentage of Dy is higher in Dy_2O_3 than Dy_2Fe_{17}, therefore, it is logical to conclude that Dy_2O_3 has a greater effect on extraction efficiency than Dy_2Fe_{17} phase.

4. Conclusions

Effect of scrap size on the recycling efficiency of RE permanent magnets in the LME process was observed. Oxygen content, which increased with decreasing particle size, was found to have a significant effect on the extraction rate. Consequently, the extraction efficiency increased with increasing particle size and increasing time. The highest extraction rate of 97% Dy was achieved in the particle size of over 2000 um for a reaction time of 48 hours. Un-extracted Dy remained in the form of Dy_2O_3 and Dy_2Fe_{17} phase. The phase fraction percentage of Dy_2O_3 decreased while Dy_2Fe_{17} phase increased with increasing particle size, making Dy_2Fe_{17} the more dominant among the two with higher phase fraction in larger particle size powders. However, the percentage of Dy in Dy_2Fe_{17} phase is low as compared to Dy_2O_3 because of which Dy_2O_3 has a greater effect on Dy extraction efficiency than Dy_2Fe_{17}. In order to achieve 100% extraction efficiency for Dy, complete reduction of Dy_2O_3 and decomposition of Dy_2Fe_{17} is required, where reduction of Dy_2O_3 remains to be the major problem. Complete reduction of Dy_2O_3 is an important topic for future research, and one possibility of achieving that is by using catalyst.

Acknowledgments

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