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EFFECT OF Mg RATIO ON THE EXTRACTION OF Dy FROM (Nd,Dy)-Fe-B PERMANENT MAGNET USING LIQUID Mg

Recently, since the demand of rare earth permanent magnet for high temperature applications such as an electric motor has increased, dysprosium (Dy), a heavy rare earth element, is becoming important due to severe bias in its production. To fulfill the increasing need of Dy, recycling offers as a promising alternative. In recycling of rare earths, Hydro-metallurgical extraction method is mainly used however it has adverse environmental effects. Liquid metal extraction on the other hand, is an eco-friendly and simple method as far as the reduction of rare earth metal oxide is concerned. Therefore, liquid metal extraction was studied in this research as an alternative to the hydro-metallurgical recycling method. Magnesium (Mg) is selected as solvent metal because it doesn't form intermetallic compounds with Fe, B and has a low melting and low boiling point. Extraction behavior of Dy in (Nd,Dy)-Fe-B magnet is observed and effect of Mg ratio on extraction of Dy is confirmed.

Keywords: Dysprosium, Liquid Metal Extraction, (Nd,Dy)-Fe-B Magnet, Extraction Behavior, Diffusion

1. Introduction

Rare earth based magnets are used in various applications due to their superior magnetic properties as compared to the other permanent magnets like ferrite or alnico magnet. Previously, Sm-Co permanent magnet was developed in 1970s to replace these magnets having excellent magnetic properties [1,2]. However, due to rising prices and instability of Sm and Co supply lead to the development of neodymium (Nd) based permanent magnet which are relatively cheap and have improved magnetic properties.

The early Nd based permanent magnets had superior magnetic properties such as BHmax and residual magnetic flux density however it couldn't be used at high operating temperature due to low curie temperature. In this regard dysprosium (Dy), which has high anisotropy coefficient, was added to improve the coercivity. Demand of Dy doped Nd based permanent magnet is increasing in industries which require high magnetic properties at high operating temperature [3-5]. But similar to Sm-Co permanent magnet, price of Nd and Dy, main elements of Nd based permanent magnet, is increasing and supply is instable due to the bias in resources as 70% of rare earths used are produced by China so the method to compensate production of rare earths has to be developed. In order to overcome the supply issue, three methods are under focus in the form of reduction, reuse and recycling of rare earths. Firstly, researchers are trying to develop high magnetic properties of permanent magnet with reduced RE contents, however, there are some difficulties to realize unique properties of rare earths. Secondly, the method to reuse magnet is also underdevelopment but magnetic properties are low because of impurities. Therefore, the third method, recycling of rare earths from magnet is of prime focus as the resultant byproduct are rare earths metals and compounds.

Hydro-metallurgical recycling method has been used mainly as the existing recycling method, however recently, research on pyro-metallurgical method are gaining more attention as an alternative recycling method due to environmental damage posed from the generated acid, base and waste water during hydro-metallurgical recycling process [6]. So liquid metal extraction, one of the pyro-metallurgical recycling methods is observed in this research, as it doesn't use chemicals and byproduct is metallic state. Therefore liquid metal extraction can be an eco-friendly process for extraction of rare earth from magnet. Therefore, hydro-metallurgical recycling method can be expected to be replaced by liquid metal extraction.

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Mg is chosen for solvent metal in this study because Mg has selective reactivity with rare earths and melting point and boiling point of Mg are lower than other material which can be solvent metal in liquid metal extraction.

Reports regarding recycling of RE magnets are generally focus to Nd diffusion to the solvent materials [7-9], but rare to Dy, although its usage to future industries keeps increasing. Nam et al reported that Dy was extracted to Mg matrix successfully from Dy-Fe-B alloy with time at 900^{o}C [10], and that the extraction of Nd among Nd-Dy-Fe-B alloy was completed until 6hours at the same temperature [9]. So understanding the effect of quantity of Mg to Nd-Dy-Fe-B seems to be important, in accordance with the phase change of Dy_2O_3 and Dy_2Fe_{17}, factors to the Dy and Mg reaction [10,11]. This investigation displays behavior of Dy extraction to Mg matrix from Nd-Dy-Fe-B alloy with the variation of Mg in quantity under microstructural aspect using a couple method as shown in Fig. 1.

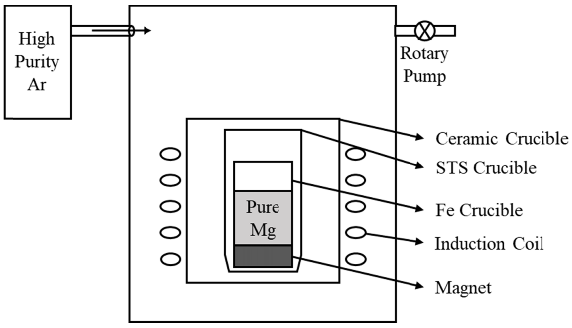


Fig. 1. Apparatus of reaction experiment

2. Experimental

39UH grade magnets with 3.5wt.% of Dy as shown in the Table 1, were used and reaction experiment was observed with Mg ratio. Dimensions of magnet were designed to have low height (10×10×1 mm) and weight (0.3 g) in order to completely extract Nd. Reaction experiment was carried out in a high frequency induction furnace (Model DTIH-0020VMF, Korea). High frequency induction furnace can give Lorentz force to circulate Mg for helping in the extraction of rare earths in magnet. Changes of phase fraction and microstructure were analyzed by image analyzer (Program, ImageJ) and scanning electron microscope (FE-SEM, Model JSM-100F) equipped with energy dispersive X-ray analysis (EDS). Images of magnet were taken by three sections, top, middle and bottom of magnet, in order to calculate phase fraction. 10 images with 500 magnification were taken in all the three sections for calculating phase fraction of Dy-oxide in grain boundaries with FE-SEM. Similarly, 10 images with enhanced magnification of 5000 were also taken in each section calculating phase fraction of Dy-Fe intermetallic compound in each grain with FE-SEM. Image analyzer calculates phase fraction of SEM images by scanning brightness of each phase. Phase fraction of each sector were almost similar because high frequency induction furnace helps circulation of Mg with Lorentz force so average phase fraction was calculated in this study. Phase transformation after reaction was observed by X-ray diffraction (XRD, Model D/Max 2500PC). Extraction efficiency is confirmed by X-ray Fluorescence Spectrometry (XRF, Model ARL PERFORM'X). Effect of Mg ratio on reaction behavior can be confirmed by these analysis.

TABLE 1

Composition of main elements in magnet

	Nd	Dy	Fe
wt.%	25.8%	3.5%	62.98%

3. Results and discussion

Main phases included rare earths in magnet are RE(Nd, Dy)$_2$Fe$_{14}$B, RE(Nd, Dy)-rich, RE(Nd, Dy)-oxide. Rare earths in magnet are diffused to Mg. In order to confirm extraction behavior of Dy specifically, experiments are designed to extract almost all of the Nd inside the magnet. Therefore, reaction experiment is observed with 6 part Mg and 1 part magnet as the starting material (W_{Mg}:W_{Magnet} = 6:1). During 6 hours at 900°C as Akahori

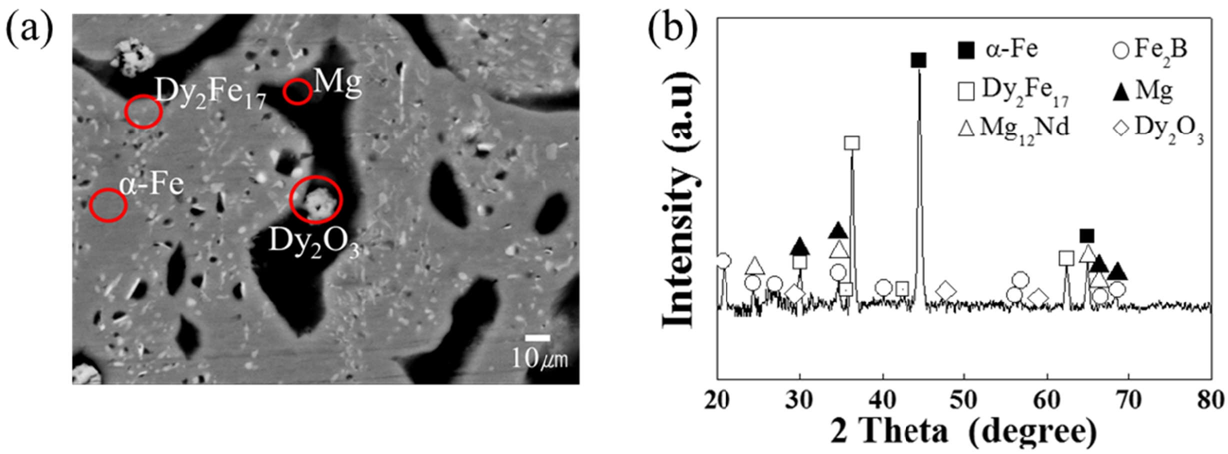


Fig. 2. (a) Microstructure and (b) XRD result of magnet after reaction between magnet and Mg with 6 times Mg ratio than magnet (W_{Mg}:W_{Magnet} = 6:1) during 6hours at 900°C

referred conditions [10], Nd is almost completely extracted. Dy included phases are identified with XRD and SEM-EDS as presented in Fig. 2. Circled white particles located in grain boundary are Dy-Oxide and needle shaped white particles located inside the grains are Dy_2Fe_{17} intermetallic compounds. Dy-oxide is expected to be generated from existing RE(Nd, Dy)-oxide in magnet because RE(Nd, Dy)-oxide is located in grain boundaries of magnet. Nd in RE-oxide reacted with Mg and diffused out but Dy in RE(Nd, Dy)-oxide higher affinity towards oxygen as compared to Nd. Consequently Dy remained unreacted. Dy_2Fe_{17} intermetallic compound is expected to be generated as a result of the reaction between $RE(Nd, Dy)_2Fe_{14}B$ and Mg. Heat of mixing index between Dy and Fe which explains the affinity during reaction is negative 3, therefore Dy_2Fe_{17} is generated. After the reaction, Fe and B remained as α-Fe and Fe_2B.

In order to extract all of rare earths inside the magnet, Dy in Dy-oxide and Dy_2Fe_{17} needs to be extracted. Akahori stated that Dy-oxide can be reduced as Mg ratio is increased because activity of Dy is lower and increasing the Mg ratio progresses the reaction between Dy-oxide and Mg [10]. Nam also confirmed the reduction behavior between Dy-oxide and Mg using thermodynamic calculation [11]. In order to decompose Dy_2Fe_{17}, Nam confirmed possibility to decompose Dy_2Fe_{17} with increasing Mg ratio by observing thermodynamic calculation between Dy_2Fe_{17} and Mg [11]. Therefore, reaction experiments are observed with Mg ratio in this research.

Reaction experiments are observed with 6 to 15 times Mg ratio than magnet (W_{Mg}:W_{Magnet} = 6:1 ~ 15:1) during 6 hours at 900°C. Fraction of infiltrated Mg is increased as shown in Fig. 3 and Fig. 4. It depends on infiltration rate of Mg and the infiltration rate follows equation 1.

$$J = \frac{J_b\delta + J_l d}{d} = -\left(\frac{D_b\delta + D_l d}{d}\right)\frac{dC}{dx} \quad (1)$$

D_l (Diffusion coefficient of Mg to grain), D_b (Diffusion coefficient of Mg to grain boundary), d (Thickness of grain), δ (Thick-

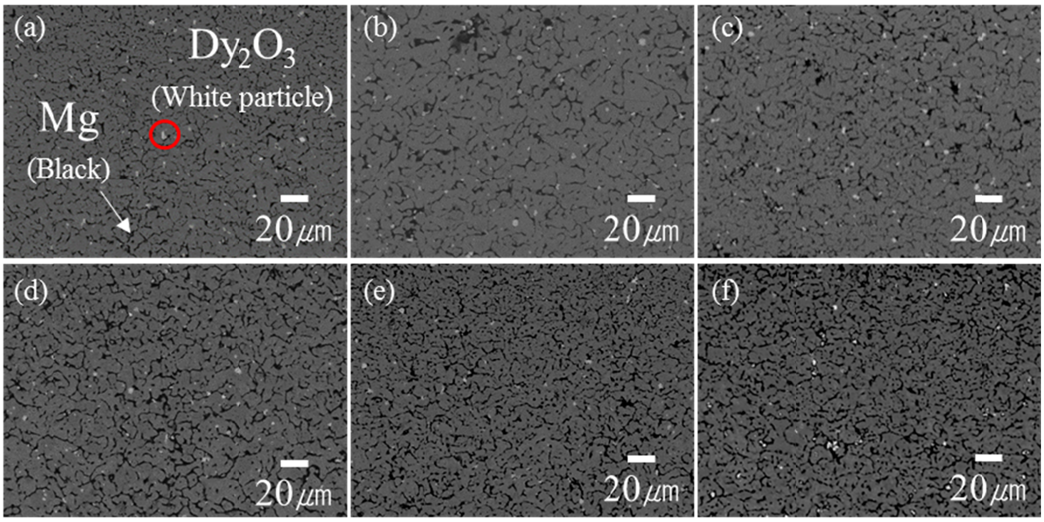


Fig. 3. Fraction changes of Dy-oxide and Mg by microstructural analysis with Mg ratio during 6 hours at 900°C. (a) W_{Mg}/W_{Magnet} = 6, (b) W_{Mg}/W_{Magnet} = 7, (c) W_{Mg}/W_{Magnet} = 8, (d) W_{Mg}/W_{Magnet} = 9, (e) W_{Mg}/W_{Magnet} = 10, (f) W_{Mg}/W_{Magnet} = 15

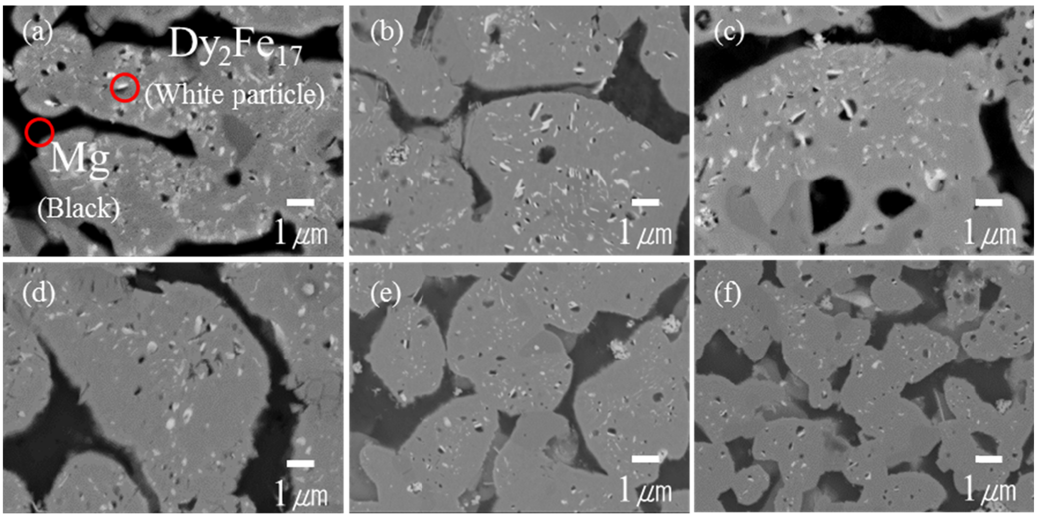


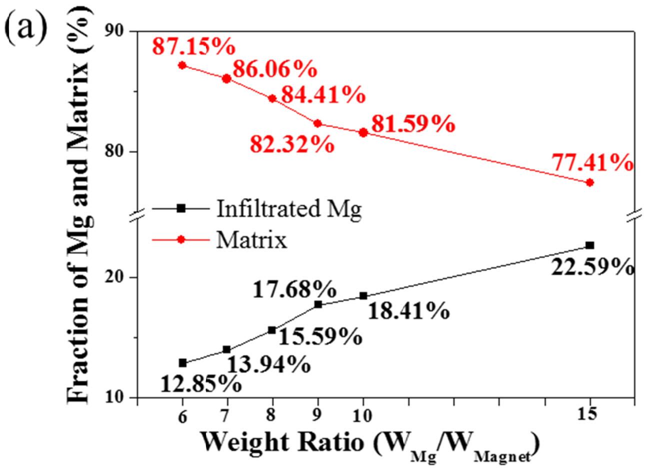
Fig. 4. Fraction changes of Dy_2Fe_{17} and Mg by microstructural analysis with Mg ratio during 6 hours at 900°C. (a) W_{Mg}/W_{Magnet} = 6, (b) W_{Mg}/W_{Magnet} = 7, (c) W_{Mg}/W_{Magnet} = 8, (d) W_{Mg}/W_{Magnet} = 9, (e) W_{Mg}/W_{Magnet} = 10, (f) W_{Mg}/W_{Magnet} = 15

ness of grain boundary) and *dx* (Distance of infiltration) are not changed because materials used in experiments are same. Infiltration rate is getting faster as Mg ratio is increased because infiltration rate depends on concentration of Mg (*dC*). Fraction of infiltrated Mg is increased while the fraction of matrix is decreased as infiltration rate of Mg is getting faster with increasing Mg ratio. This is indicated in Fig. 5 by image analysis of Fig. 3 and Fig. 4. Therefore, it is confirmed that amount of infiltrated Mg is increased with Mg ratio.

As shown in Fig. 5, width of infiltrated Mg is increased confirming that the Mg follows high-diffusivity path. It means that Mg infiltrates both grain and grain boundary. Therefore, Dy-oxide located in grain and Dy_2Fe_{17} located in grain boundary react with Mg. Dy-oxide is reduced and Dy_2Fe_{17} is decomposed as amount of infiltrated Mg is increased as shown Fig. 3 and 4. Nd is not detected by SEM-EDS because Nd is almost completely extracted by Mg. Dy-oxide located in grain boundary is reduced and Dy_2Fe_{17} located in grain is decomposed by Mg ratio. It is shown in Fig. 6 by image analysis of Fig. 3 and Fig. 4. Dy is diffused out by Mg ratio as shown in Fig. 7.

4. Conclusions

Even if Nd and Dy are extracted at the same time, in order to extract all of rare earths in magnet, Dy has to be extracted completely because Dy is extracted slowly as compared to Nd. The extraction of Dy is slow due to the Dy remained in the form of Dy-oxide and Dy_2Fe_{17} intermetallic compound due to its high affinity with oxygen and Fe during the reaction. However it is has confirmed in previous research by using thermodynamic calculation that Dy-oxide and Dy_2Fe_{17} have a possibility to react with Mg if the Mg ratio is increased. The thermodynamic prediction was confirmed in this as we increased the Mg ratio, infiltration rate gets higher because as it depends on the total Mg concentration. It is also confirmed that Mg is infiltrated both grain and grain boundary through observing the width of the infiltrated Mg by Mg ratio. Therefore, Dy in Dy-oxide and Dy_2Fe_{17} is diffused out to Mg as amount of infiltrated Mg is increased. Finally Dy is diffused more by higher Mg ratio and extraction efficiency of Dy reached to 66%.



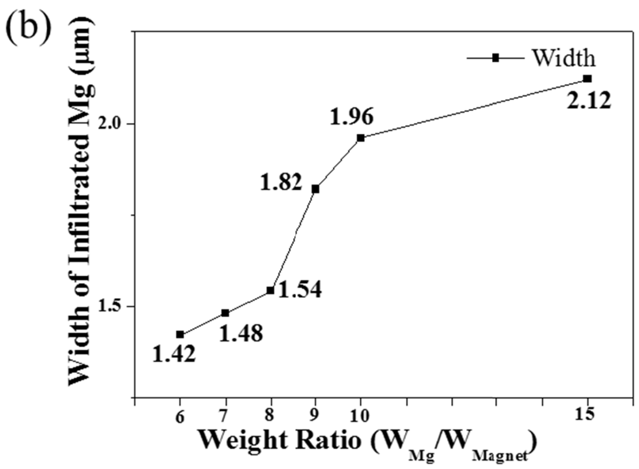


Fig. 5. Infiltration behavior of Mg with Mg ratio using image analysis. (a) Fraction of Mg and matrix with Mg ratio, (b) Width of infiltrated Mg with Mg ratio

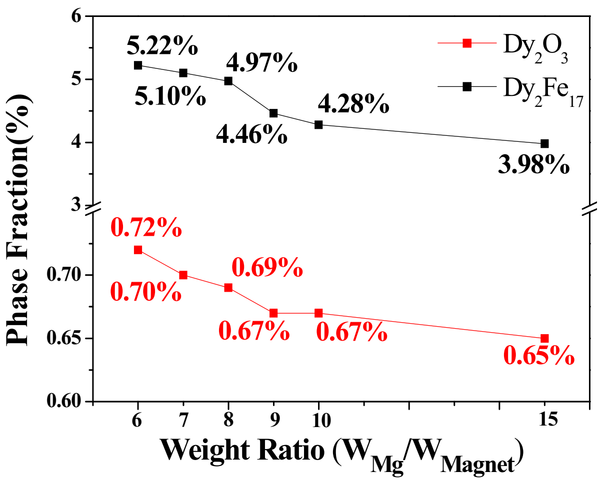


Fig. 6. Fraction of Dy-oxide and Dy_2Fe_{17} with Mg ratio using image analysis

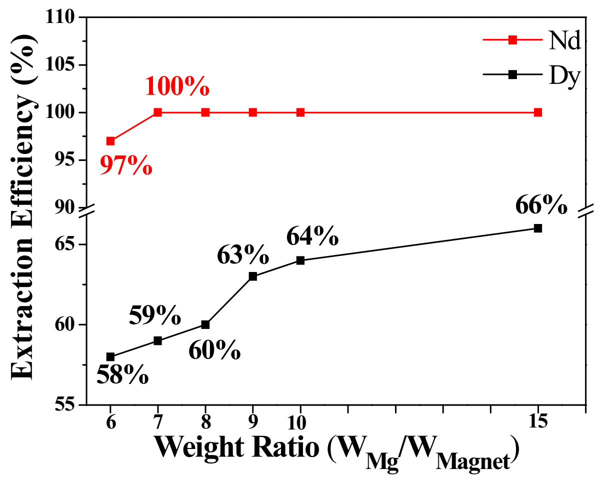


Fig 7. Extraction efficiency of rare earths

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