IMPROVEMENT OF MAGNETIC PROPERTIES OF MELT-SPUN PRODUCED $Nd_2Fe_{14}B$ PARTICLES DURING SURFACTANT-ASSISTED BALL MILLING

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ABSTRACT: NdFeB permanent magnets are used for variety of applications such as electronics, automotive and clean technology industries. The majority of commercial NdFeB permanent magnets are produced by melt-spinning techniques and sintering. The sintered NdFeB magnets represent about 90% of the total rare earth permanent magnet market. Sintered melt-spin NdFeB magnets exhibit the highest magnetic performance due to their strong crystallographic alignment. These magnets have enabled their applications to operate with the highest energy efficiencies and to be fabricated in the most compact form. In this study, the flaky shaped $Nd_{15}Fe_{77}B_8$ magnetic alloy powders were produced by melt-spinning technique. In this process, the powders were produced by using a single roller melt spinning apparatus with high vacuum atmosphere (10^{-7} mbar). The flaky shaped $Nd_{15}Fe_{77}B_6$ powders were milled by using the high energy ball milling under vacuum atmosphere with surfactant-assisted material. The experiments were performed to optimize the milling parameters regarding the particle size and magnetic properties of the powders.

Key words: $Nd_{15}Fe_{77}B_8$ magnetic alloy, Melt spinning, Surfactant-assisted)

INTRODUCTION

The NdFeB magnets with excellent properties have extended the applications in the field of motors such as hybrid electric vehicles and electric vehicles. In recent years, there is a trend of permanent magnet motors replacing traditional motors, because they have high efficiency and can run on lower energy. Therefore, the sintered NdFeB magnets with high coercivity have much appeal for the scientist and engineers (Yan et al., 2011). There are two major commercialized process routes for the production of NdFeB permanent magnets. The first method is powder metallurgy and the second one is the melt spinning process. The majority of commercial NdFeB permanent magnets are produced by powder metallurgy and melt-spinning techniques. In recent years, the melt spinning technique has attracted rapidly increasing interest in NdFeB alloys because it can be used to produce reliable materials for bonded magnets or to directly produce thin plate-shaped, permanent magnets for diverse applications (Tian et al., 2004). This process is used to make rapidly solidified microcrystalline and amorphous alloy ribbon, flake, etc. Moreover, it is possible to obtain a supersaturated solid solution with a higher quantity of alloying elements, and to avoid or minimize the formation of second phases. Sintered melt-spin NdFeB magnets exhibit the highest magnetic performance due to their strong crystallographic alignment. These magnets have enabled their applications to operate with the highest energy efficiencies and to be fabricated in the most compact form (Brown, Wu, He, Miller, & Herchenroeder, 2014). There are many factors that govern the suitability of a permanent magnets such as coercivity, high remanence (B_r) and maximum energy product ($(BH)_{max.}$). These hard magnetic properties strongly depend on the mean particle size of the NdFeB powders. This dependence is a result of interactions: smaller the mean powder size, higher the coercivity (Szymura, Wyslicki, Rabinovich, & Bala, 1994). High energy ball-milling is a simple, inexpensive and efficient technique for the size reduction of micro or nanocrystalline powders (Neu & Schultz, 2001; Ono et al., 2002). The main advantage of the ball milling method is the applicability of this method to large scale production. and high purity of the powders. On the other hand, this method hosts some deficiencies in term of the purity of the powders. In this sense, the oxidation of the milled powders is main concern because it affects the subsequent process steps such as pressing, sintering and the magnetic properties of resultant product (Chandrasekaran, 2007). For this reason, it is essential to use protective agents during high energy ball milling process to avoid the oxidation of the powders. It has been reported that the rare-earth intermetallic compounds powders were ball milled in the presence of an organic liquid and surfactants, and this method is called as surfactant assisted ball milling (SABM) (Simeonidis et al., 2011). This technique has become a novel approach for the preparation of NdFeB particles and flakes (Su et al., 2013). Surfactants help to decrease the particle size and facilitate shape homogeneity during the milling process. Surfactant agents have also important chemical protection and lubrication to the powder surfaces. In this regard, the surfactant helps to decrease local heating, contamination and oxidation of the powders (Simeonidis et al., 2011).

In the present study, we have investigated the changes in size, morphology, thermal and magnetic properties of magnetically hard $Nd_{15}Fe_{77}B_8$ alloy powders by using a surfactant assistant high energy ball milling method.

METHODS

Commercial magnetic alloy ingot with nominal composition of $Nd_{15}Fe_{77}B_8$ (at %) was used to produce flaky shaped powders. The rapidly solidified $Nd_{15}Fe_{77}B_8$ alloy powders have been produced by using a laboratory scale single roller melt spinning device operating in high vacuum atmosphere (10^{-7} mbar). Small amounts of the crushed ingots were placed in a hexagonal boron nitrite crucible with slit shape nozzle of 10x0,7 mm at the bottom. The ingots were induction melted and superheated to about 1350 °C in a vacuum atmosphere. The temperature of the melt was monitored by infrared thermometer. The molten alloy was ejected through slit shape nozzle with compressed argon gas of 0,25 bar onto rotating cooper wheel (27 cm diameter) at a surface velocity of 52 m/s (maximum speed of wheel) under vacuum atmosphere. Milling process of the rapidly solidified flaky shaped powders by melt spinning method was performed in an atmosphere of oxygen free inert environment (vacuum atmosphere, 10^{-3} mbar) with addition of protective surface active agents. The oleic acid (99,9 purity) was used as surfactant and heptane and hexane (99,9 purity) were added as an organic solvent during milling process. Fritsch Pulverisette 6 type high energy ball miller was used and the flaky shaped powders were ground in a 250 ml capacity milling jar made of tool steel and boron-carbide surface hardened. 5 mm diameter tungsten carbide balls were used and the rotational speed of the jar was kept constant as 300 rpm. The weight ratio of the balls to the powders ($\mu = m_{ball}/m_{powders}$) was 10:1. The amounts of surfactant and organic solvent used were about 10 – 12% by weight of the starting powders and milling times were varied from 1,5 to 6,5 hours. After the milling process, the slurry mixture of powders and surfactant material were obtained. Cleaned powders were achieved with the processes of washing with ethanol and centrifugal drying.

The phase structured of the sample was examined by x-ray diffraction (XRD) at room temperature using PANalytical X'pert^3 Powder diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) was employed to examine the morphology, mean particle size and microstructure of the particles. The magnetic properties of particles were measured by Physical Properties Measurements System (PPMS) equipment with 9 T vibrating sample magnetometer (VSM).

RESULTS AND FINDINGS

The melt spinning is a method of producing rapidly solidified ribbons. However, Nd-Fe-B alloy powders, instead of ribbon were produced by melt spinning method because brittle character of the $Nd_{15}Fe_{77}B_8$ alloy, in this study. Morphology of produced $Nd_{15}Fe_{77}B_8$ magnetic alloy powders by melt spinning method is seen

in Fig. 1.a. As can be seen from the figure, the shape of the produced powders is characterized by irregular and flake form (Yan et al., 2011). The flaky shaped powders have 25-100 µm width and 80-600 µm length. The thickness of these particles varied between 5-48 µm. The microstructure of the $Nd_{15}Fe_{77}B_8$ alloy powders produced by the melt spinning method was given in Fig.1.b. Predominant shape of the microstructure was equiaxed cellular and the mean cell size was decreased with decreasing powder size and decreasing the thickness of the flaky shaped powders. The mean cell sizes for 5 and 48 µm powders were measured as 0.69 µm and 1.3 µm, respectively. There is a direct relationship between microstructural grain size and cooling rate for the produced powders. The cooling rate increases with decreasing cell size.

For calculation of the cooling rate of the powders, the equation given in (Ozawa, Saito, & Motegi, 2004) was used. The cooling rates of 5 and 48 µm thick flaky shaped powders were calculated as $4.3x10^{-6}$ K/s and $4.7x10^{-5}$ K/s, respectively. Besides microstructural examinations of produced powders, EDX analysis was also made to reveal the phase structures of the powders. Fig. 1.b shows the back-scattered microstructure of produced powder. As can be seen from Fig.2, the micrograph exhibits the dark equiaxed grain matrix together with the white grain boundary. The present of phases was identified by virtue of EDX analysis According to the EDX analysis, the matrix consists of $Nd_2Fe_{14}B$ hard magnetic phase located in grain interior and the grain boundary is the Nd-rich phase which is soft magnetic properties. From the EDX analysis the elementel composition of grain interior by wt. percentage are 27.58% Nd, 62.44% Fe and 9.98% B. These values indicate the nominal composition of magnetically hard $Nd_2Fe_{14}B$ phase.

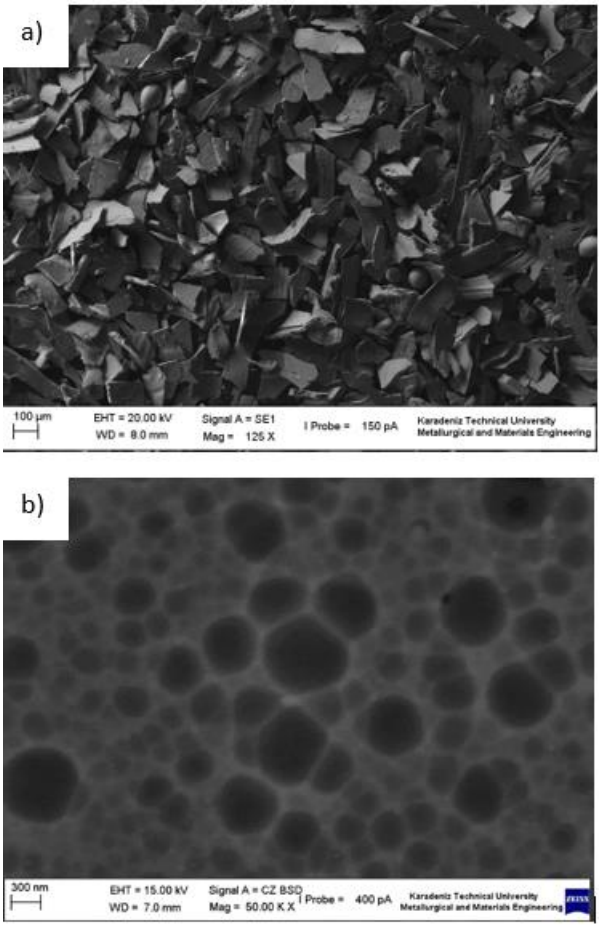

Figure 1. a) rapidly solidified of NdFeB powders by melt spinning method, b) Microstructure of $Nd_{15}Fe_{77}B_8$ magnetic alloy ribbons.

The XRD pattern of the unmilled flake powders are presented in Figure 2. As can be seen, produced flaky powders mainly consists of $Nd_2Fe_{14}B$ hard magnetic phase. Besides this phase, magnetically soft α-Fe (primer iron) and Nd-rich phases were observed in small quantity in the melt spun powders. The α-Fe phase is often found in Nd-Fe-B system alloys, because the $Nd_2Fe_{14}B$ phase is formed by peritectic reaction of liquid and the primary α-Fe phase.

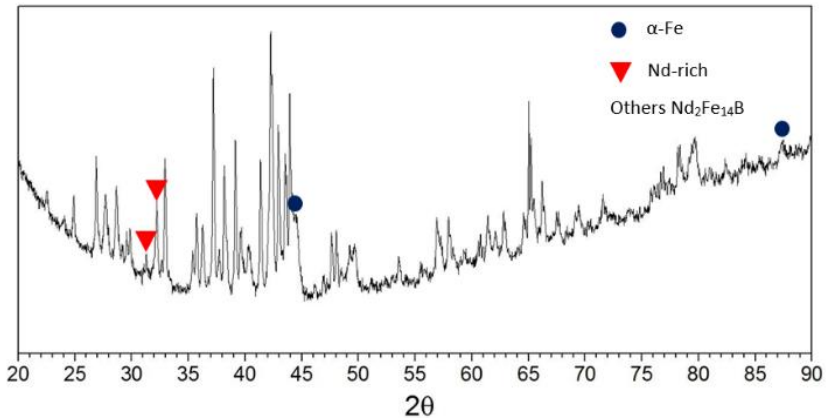

Figure 2. Diffraction pattern of $Nd_{15}Fe_{77}B_8$ magnetic flake powder.

Figure 3. shows the SEM micrographs of the high energy ball milled $Nd_2Fe_{14}B$ particles obtained with various milling times. As stated above, only milling time was changed while other parameters were kept constant. The powders were milled for six different milling times of 90, 150, 210, 270, 330, 390 min in the oleic acid environment. As can be seen from the figure, the particles agglomerated with increasing milling time and decreasing particle size. In the high energy ball milling, the large particles break as a result of the internal strain created by the high pressure exerted on the particles. On the other hand, the finely divided particles tend to agglomerate in order to minimize their surface energy. But, the presence of solvent and surfactant in SABM is known to be very efficient at preventing cold welding and the agglomeration of particles during ball milling. Surfactant covering a particle or flake can lower the surface, enabling long-range capability forces and lowering the energy required for crack propagation (Lewis, Panchanathan, & Wang, 1997).

The internal strain in the particles increases rapidly at the beginning of the ball milling, so large sized micro or nanocrystalline powders produced by melt spinning method break into tens of micrometers or micro sized irregular particles. Then, micro cracks start from an easy cleavage plane in the particles and the grain. At the edge of the grain, the development of micro crack is prevented due to crystal mismatch between grains. The micro crack could spread through the grain boundary into the adjacent grains until the internal strain concertation is sufficiently high (Su et al., 2013).
The variation of mean particle size with milling time was given in Fig. 4. As can be seen, the mean particle size decreased with increasing milling time. The mean particle sizes obtained are 1.481, 1.214, 0.948, 0.872, 0.431 and 0.266 μm for 90, 150, 210, 270, 330, 390 min. milling times, respectively.

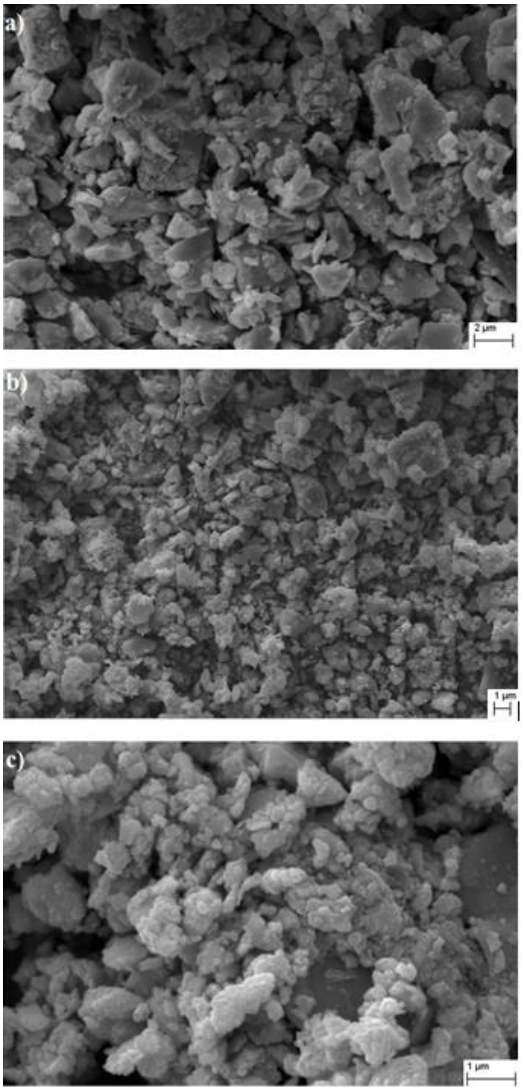

Figure 3. SEM images of NdFeB powders obtained by ball milling with various milling times: a) 90 min., b) 210 min. and c) 390 min

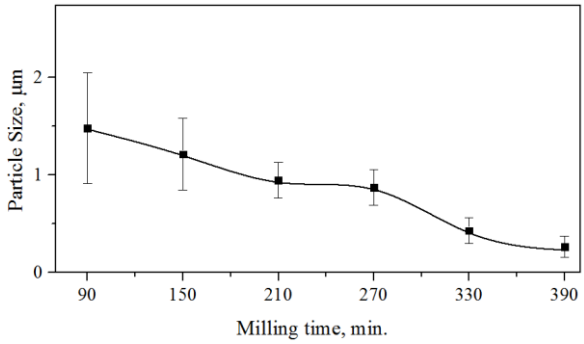

Figure 4. Effect of ball milling time on the mean particle size of the NdFeB powders.

Magnetic hysteresis loops were recorded for the starting powder and different milling times in Figure 6. The coercivity of the Nd-Fe-B alloys is not only heavily dependent on the grain size of the $Nd_2Fe_{14}B$ phase but also on the amounts of the soft magnetic phases such as α-Fe phase and Nd-rich phase. The appearance of irregularities in the hysteresis of the unmilled flake powders by melt spinning

process is attributed to the presence of the soft magnetic phases of Nd-rich and α-Fe.

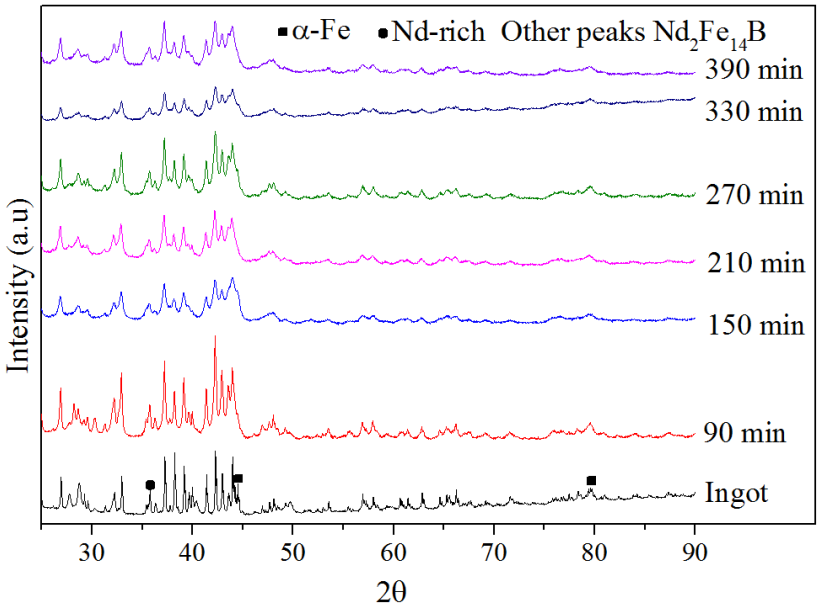

Figure 5. XRD pattern of the starting ingot magnetic alloy and milled powder with various times.

Figure 7. illustrates the variation of coercivity with milling time from 90 to 390 minutes. The figure shows the coercivity increase with increasing milling time. The maximum coercivity (4.250 kOe) is attained after 330 minutes. Further increase of SABM time leads to the decrease of coercivity following the evolution of particle isolation and the dimension reduction. According to literature, at high milling periods, the magnetic anisotropy of the powder is reduced by the time. However, the presence of the elongated particles shape anisotropy (Rong, Poudyal, & Liu, 2010; Simeonidis et al., 2011)

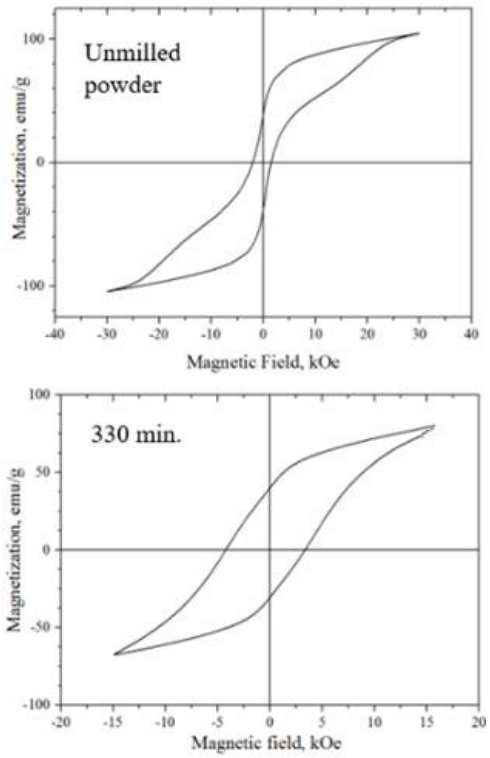

Figure 6. Hysteresis loops of the unmilled flake powders and after SABM for 330 minutes.

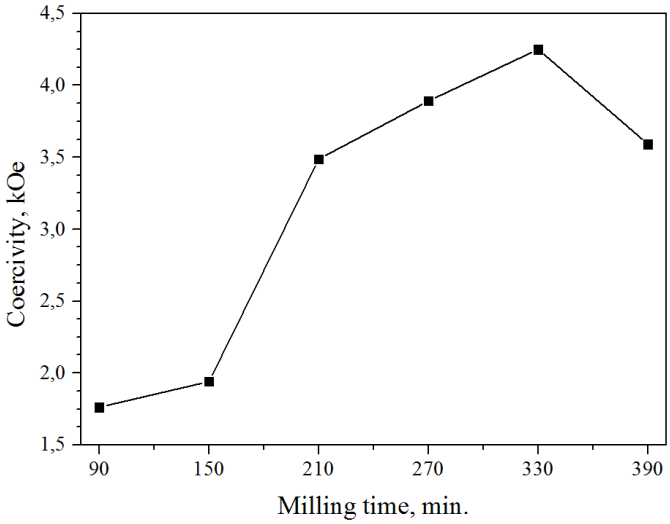

Figure 7. Coercivity of powder as a function of the different SABM times.

CONCLUSIONS

1. The mean cell sizes of produced flaky shaped powders by melt spinning method were increased with decreasing cooling rate.
2. The mean particle size of milled powders decreased with increasing milling time.

3. According to XRD analysis, the diffraction peaks of the $Nd_2Fe_{14}B$ hard magnetic phase are observed in all samples produced with SABM. Besides that, soft magnetic phases of Nd-rich and α-Fe are observed in samples.
4. The coercivity of milled powders increase with increasing milling time. The maximum coercivity is attained after 330 minutes. increase of SABM time leads to the decrease of coercivity following the evolution of particle isolation and the dimension reduction.

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