Crystal structure and magnetic properties of $Nd_2Fe_{14}B$ powder prepared by using high energy milling from elements metal Nd,Fe,B powders

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Abstract. The $Nd_2Fe_{14}B$ powder has been made by using High Energy Milling (HEM) from mixed metal powders Iron (Fe), Neodymium (Nd) and Boron (B). The Nd, Fe and B powders were mixed according stoichiometric composition (atomic ratio Nd:Fe:B = 2 : 14 : 1) and milled and milling time was varied in 10, 20, and 40 hours by using HEM. Toluene liquid was used as milling media to protect of metal powders from oxygen. The measurement result of x-ray diffraction show that the optimum $Nd_2Fe_{14}B$ phase already formed about 69,46 % after milling 40 hours with crystallite size about 25.64 nm. The magnetic properties of milled powders were measured by using VSM at room temperature. The highest value of magnetic properties are obtained at powder milled in 40 hours, at this condition, it is obtained Ms = 122 emu/g, Mr = 81 emu/g, Hc = 5.54 kOe and BHmax = 11.01 MGOe.

1. Introduction

The demand of NdFeB magnets has increased rapidly in various fields of life since their development in 1984, due to their excellent magnetic performance [1]. The $Nd_2Fe_{14}B$ is one type of permanent magnet based rare earth metals, that the $Nd_2Fe_{14}B$ magnet has high magnetic properties [1]. The $Nd_2Fe_{14}B$ magnets are required by many electric motor industries, automotive industries, industrial electronics, and industrial electricity generator [2,3]. $Nd_2Fe_{14}B$ compound formed from the reaction between powder Neodymium (Nd), iron powder (Fe), and powder Boron (B). There are several technologies to make $Nd_2Fe_{14}B$ powder that the process is generally through the smelting process at high temperature (1700 - 1800 ° C) and the atmosphere of process isolated by inert gas such as nitrogen or argon [4,5] . With this technology, it needed a large electrical energy and high cost for production, and the technical operations are quite difficult. On the basis of the conducted an alternate way, another to make the compound $Nd_2Fe_{14}B$ with costs lighter and easier production, namely with using mechanical alloying techniques where powder Nd, Fe, and B as raw materials are mixed and milled using high energy milling (HEM) with high-speed 4000 - 5000 rpm [5]. Some of Authors have been done mechanical alloying process to produce of $Nd_2Fe_{14}B$ powder with using ball mill in Hydrogen gas atmosphere [6,7]. During milling process has been going on repeating the process of mechanical mixing, cold welding, fracturing, and rewelding powders which can lead to a reduction in particle size, and a milled powder becomes more reactive[6]. The existing atoms (Nd, Fe, B) in starting materials will easily vibrate during milling to facilitation the surface diffusion resulting in a phase transformation into $Nd_2Fe_{14}B$ phase [7,8]. Through the process of mechanical alloying by means of milling to note the atmosphere, because Nd and Fe metals are very easy to interact with oxygen so easily corroded at room temperature. Due to the corrosion problem in the milling process , toluene liquid is used as media so that the powder Nd and Fe can be isolated from oxsigen during the milling process. This research was conducted on the process of synthesis of $Nd_2Fe_{14}B$ powder from mixed of elements metal powders (Nd,Fe,B) by using High Energy MIlling. The purpose of this research to determine the relationship between milling time with percentage of $Nd_2Fe_{14}B$ phase formation and crystal size. Besides, it was also analyzed the magnetic properties by using vibrating Sample Magnetometer (VSM).

2. Experimental

The $Nd_2Fe_{14}B$ was made at stoichiometric composition (atomic ratio of elements Nd: Fe: B = 2: 14: 1) by using mechanical alloying (MA) process. NdFeB powder is made from a mixture of raw material powders Nd with a purity of 99.90% and 200 µm, Fe with a purity of 99.90% and 100 µm and Boron with a purity of 99.90% and 50 µm. Applied MA is through the process of High Energy Milling (HEM) with rotation speed 3000 rpm. Toluene is used as liquid media to protect of corrosion on metals powder Nd,Fe and B. Total weight of raw materials were 15 g consisting of a mixture of Neodymium (Nd), iron (Fe) and Boron (B). Powder Nd, Fe and B were inserted in a vial and toluene is added as much as 15 ml and added steel ball about 120 g, furthermore vial tube was closed and began the milling process. The powder preparation from upload materials to vial tube until closing the vial tube have been done in Glove Box at vacuum condition (P vac = 10 mbar). Subsequently tube vial containing the raw material was placed on a milling machine (HEM), then the HEM engine was operated with a variety of milling time, namely 10, 20 and 40 hrs. The all samples after milling process were analyzed crystal structure by using X-ray diffraction and measured magnetic properties by using Vibration Sample Magnetometer (VSM). The crystallite size of $Nd_2Fe_{14}B$ phase was calculated by using the equation of Scherrer.

3. Results and Discussion

The results of x-ray diffraction measurements of the mixture Nd- Fe-B before milling as shown in figure 1. According the XRD patterns and JCCPDS file as seen at figure 1 show that the mixture does not contain impurities, and only consisted of the phase Nd and Fe. The XRD peaks of Nd and Fe can be obtained by comparing the experiment peaks with reference peaks data (JCCPDS) of Nd, Fe and B.

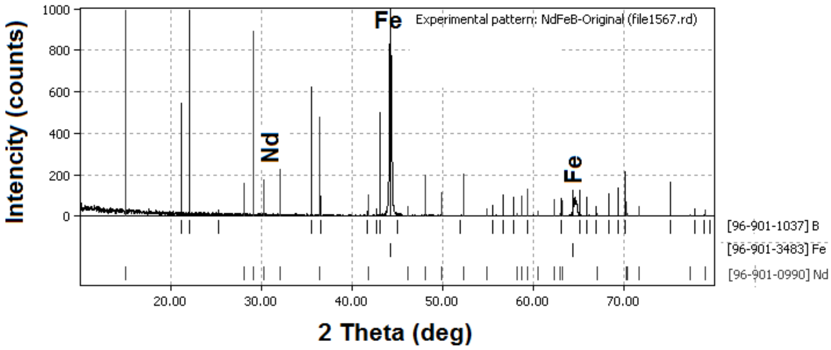

Figure 1. XRD patterns of mixed raw materials before milling.

Boron phase does not appear, it is because the amount of boron to small, so the boron phase was not detected by XRD. Next is the process of milling with milling time variations are: 10, 20 and 40 hours. Figure 2 is shown X-ray diffraction patterns of the sample that has been in the milling for 10 hours.

The refinment and peaks search were done by using software Rietveld and it was found that the peaks around the corner (2θ) : 42.94^o and 49.62 which it is an $Nd_2Fe_{14}B$ phase. The XRD curve at figure 2 has fitting value such as : wRp = 25.73, Rp = 20.29 dan χ^2 (*chi-squared*) = 1.377. The result of this refinement produces excellent quality fitting with very small R factor as well. R factor is the criteria of fit and χ^2 factor is the goodness of fit and value of χ^2 (chi-squared) were allowed a maximum of 1.3 [9]. The Results refinement of x-ray diffraction pattern by software Rietveld shows that the composition of $Nd_2Fe_{14}B$ phase is about 13:53%.

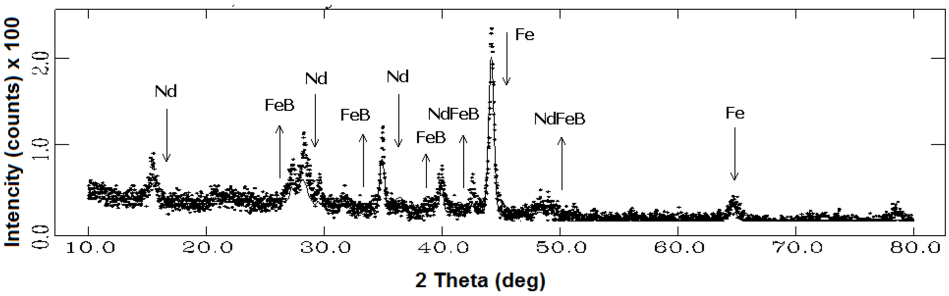

Figure 2. XRD patterns of sample after milling for 10 hrs

It is thought the majority of phases had already begun to react to each other to form alloys. The growth of $Nd_2Fe_{14}B$ phase is followed by growth of FeB phase, so the reaction that occurs after the milling for 10 hours as the equation (1)

$$2Nd + 14Fe + B \;==== 0.14\, Nd_2Fe_{14}B + 5.02FeB + 0.38Nd + 9.78Fe \qquad (1)$$

XRD analysis of sample that has been in the HEM for 20 hours is shown in figure 3. The refinment and peaks search for sample with 20 hours milling were done by using software Rietveld and the results show that a decline in the peak of Nd and FeB respectively by 3.56% and 4.48%, while the growth of $Nd_2Fe_{14}B$ become more significant about of 41.65%. The XRD curve at figure 3 has fitting value such as : wRp = 34.40, Rp = 25.08 dan χ^2 (*chi-squared*) = 1.345. According to the XRD curve as seen at figure 3 shows that the $Nd_2Fe_{14}B$ phase at sample after 20 hrs milling increases and FeB phase decreases.

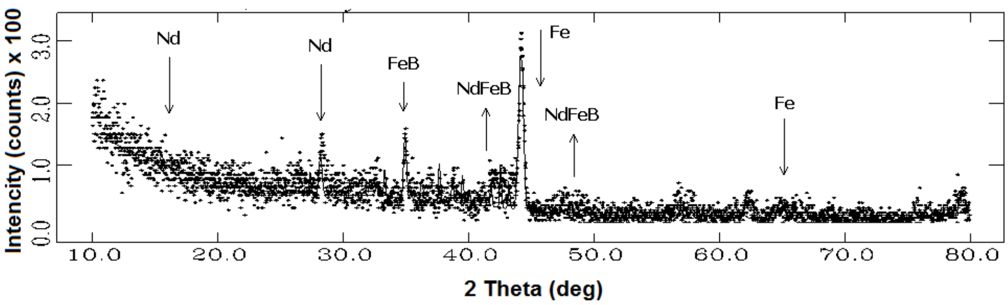

Figure 3. XRD patterns of sample after milling for 20 hrs

Figure 4 shows X-ray diffraction patterns of the sample that has been in the milling for 40 hours. The refinment and peaks search for sample with 40 hours milling were done by using software Rietveld. The XRD curve at figure 4 has fitting value such as : wRp = 33.63, Rp = 25.31 dan χ^2 (*chi-squared*) = 1.365. It has been found that the mostly $Nd_2Fe_{14}B$ phase has been formed, although still leaving phase Nd, Fe, and FeB. From the results of refinement X-ray diffraction pattern shows that the last mmixture is composed of phase $Nd_2Fe_{14}B$, Nd, Fe and FeB according to the following equation (2).

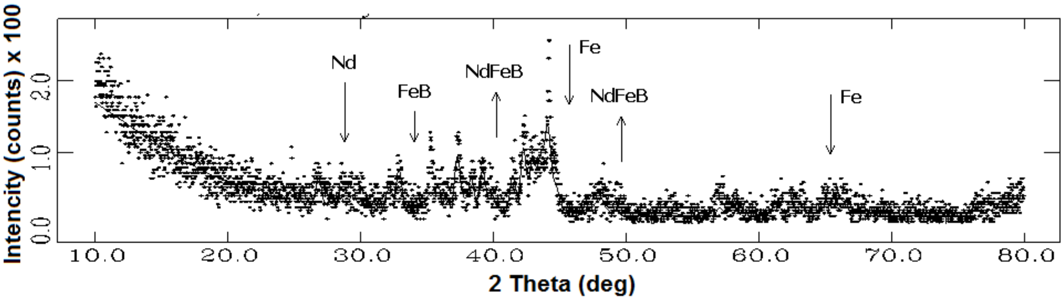

Figure 4. XRD patterns of sample after milling for 40 hrs

$$0.42Nd2Fe14B + 0.73FeB + 0.27Nd + 9.74Fe === 0.69Nd2Fe14B + 0.4FeB + 0.08Nd + 5.22Fe \quad (2)$$

These results show that the longer the process of milling the mass fraction of $Nd_2Fe_{14}B$ phase increases. The $Nd_2Fe_{14}B$ phase grows very well at $2\theta = 42^o$. The refinement of the results of x-ray diffraction pattern for a 40-hour milling results showed that a decline peak Nd and FeB respectively by 1.11 % and 2.47%, while the growth of of $Nd_2Fe_{14}B$ phase become more significant about of 69.46%. The combine curve of XRD results from different milling time is shown in figure 5 . The forming of $Nd_2Fe_{14}B$ phase is begun at sample after 10 hrs milling at $2\,\theta = 42.94^o$ and 49.62^o.

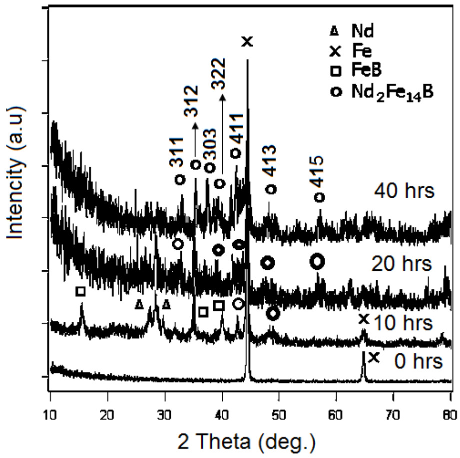

Figure 5. The combine XRD result of samples with different milling time.

The five peaks of $Nd_2Fe_{14}B$ phase look seemed to appear at $2\,\theta = 32.25^o$, 39.72^o, 42.94^o, 49.62^o and 57.26^o in sample that had been in the milling 20 hours and seven peaks of $Nd_2Fe_{14}B$ phase are found at $2\,\theta = 32.25^o$, 35.40^o, 37.77^o, 39.72^o, 42.96^o, 49.62^o, 57.26^o in sample that had been in the milling 40 hours. Milling time by using HEM can contribute significantly to the formation of $Nd_2Fe_{14}B$ phase. Energy produced during the milling process is sufficient to react the elements Nd, Fe and B to form the $Nd_2Fe_{14}B$ compound according to equation 1 and 2. The $Nd_2Fe_{14}B$ phase growth curve versus milling time obtained through MA process by using HEM is shown in figure 6. The amount of % $Nd_2Fe_{14}B$ phase increases significant with increasing of milling time. The milling process by using HEM is useful for formation of metal alloy $Nd_2Fe_{14}B$. During the milling process, that the mixed powder (metal Fe, Nd, B) became finer and more active and the reaction between metals powder can be easy without addition heat from outside.

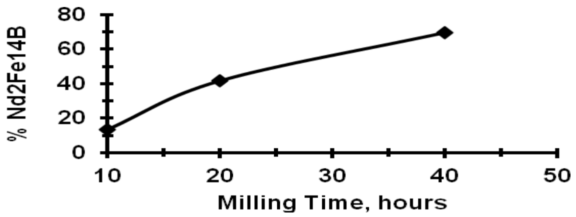

Figure 6. The relationship curve of $Nd_2Fe_{14}B$ phase formation to milling time

These experiment results show that the $Nd_2Fe_{14}B$ alloy can be produce by MA from elements metal powder for minimum 10 hrs milling time. L Sshultz and et all have been doing mechanical milling of mixture Nd, Fe and B for 30 minutes by using planetary ball mill, but $Nd_2Fe_{14}B$ phase can not be formed, and the phase $Nd_2Fe_{14}B$ can only be formed after a heat treatment at a temperature of 600°C [9]. Tetsuji Saito reported that production $Nd_2Fe_{14}B$ alloys by MA, the milling process was used HEM in H_2 atmosfir for 2 hrs and continued with heat treatment at 973K [10]. The authors [3, 9,10] have done some MA process using mechanical miling (HEM or planetary ball mill) in short time milling and limited only to result in a fine powder, and the forming of $Nd_2Fe_{14}B$ alloy is done by heat traetment. That is different with this conducted experiment, where alloying process was done by using HEM for long milling time , it shoud be more than 10 hrs. At this condition, the forming reaction of $Nd_2Fe_{14}B$ alloy can take place easily without additional heat treatment process. The crystallite size (*L* in nm) of $Nd_2Fe_{14}B$ phase were calculated from most intense peaks in XRD patterns using the Scherrer equation 3.

$$L = \frac{k\ \lambda}{B\ \cos\theta} \qquad (3)$$

Here, “k” is Scherrer constant and its value is ‘0.94’ for our material, ‘B’ is full width at half maximum (FWHM) of respective peaks, ‘θ’ is Bragg’s angle and ‘λ’ is wavelength of Cu-k α radiation (1.5406 Å) used during the XRD analysis of the samples [1]. The calculated value of crystallite size of $Nd_2Fe_{14}B$ samples with different milling time are given in table 1. Calculation of the crystallite size of $Nd_2Fe_{14}B$ each milling time was done at 2 tetha = 42.96°.

Table 1. Value of crystallite size of $Nd_2Fe_{14}B$

Milling time , hours	**Crystal Size, nm**
10	72.35
20	48.72
40	25.64

According the result of calculated crystallite size, that crystal size is enough small in range 25.64 to 72.35 nm. The crystal size of powder alloy $Nd_2Fe_{14}B$ decreases with increasing of milling time by using HEM. The magnetic properties of sample powder after milling process by using HEM were measured by using VSM. The VSM results are shown in figure 7 and table 2. It can be found that magnetic saturation Ms, moment magnetic (remanence) Mr, coercivity Hc and energy product BHmax strongly depend on milling time. Figure.7 shows that Ms, Mr and Hc increase with increasing milling time. The increasing magnetic properties due to growth of $Nd_2Fe_{14}B$ phase, where the milling time increases so the growth of $Nd_2Fe_{14}B$ increases also. The value of magnetic properties relationship with milling time is presented in table2. Sample powder with milling time 40 hours by using HEM has highest value of magnetic properties, where the amount of $Nd_2Fe_{14}B$ phase is about 69.46 % and it has Mr value = 81 emu/g, Ms =122 emu/g, Hc = 5.54 kOe and BHmax = 11.01 MGOe. The results of the magnetic properties (Mr, Ms, Hc and BHmax) of NdFeB alloy powder obtained from this research through MA were slightly higher than the results achieved by other authors who use the technique microwave assisted combustion process [11].

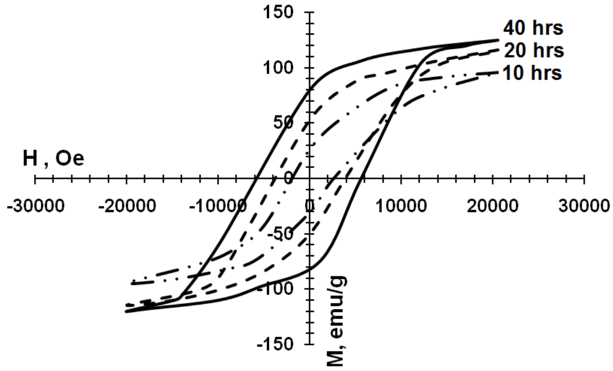

Figure 7 . Magnetic hysteresis loops of the powders after milling by using HEM

. **Table 2.** Value of magnetic properties of powders after milling by using HEM.

Milling Time	Ms, emu/g	Mr, emu/g	Hc, kOe	BHmax, MGOe
10 hours	95	28	2.41	0.55
20 hours	114	53	3.82	5.5
40 hours	122	81	5.54	11.01

4. Conclusion

The $Nd_2Fe_{14}B$ alloy powder can be made through mechanical alloying by using HEM for 40 hours milling, and in these conditions, the $Nd_2Fe_{14}B$ alloy powder was obtained as much as 64.96% with crystallite size about 25.64 mm. The value of magnetic properties tend to increase with increasing milling time, the highest magnetic properties were achieved on the powder in the milling 40 hours namely: Ms = 122 emu/g, Mr = 81 emu/g, Hc = 5.54 kOe and BHmax = 11.01 MGOe.

5. References

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