Influence of Dy-doping in Nd$_2$Fe$_{14}$B on its structural and magnetic properties

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Abstract. Study about Influence of Dy-doping in Nd$_2$Fe$_{14}$B on its structural and magnetic properties have been performed. The combination of Nd$_2$-xDy$_x$Fe$_{14}$B with x= 0.00, 0.33, 0.67, and 1.00 were using the conventional method of arc melting. The result of ingot then milled and compacted to produce a permanent magnet sample. The results of phase analysis with XRD show that the sample contained 3 phases, namely Nd$_2$Fe$_{14}$B, Fe, and Nd with dominant phase above 50% is Nd$_2$Fe$_{14}$B. Magnetic properties was measured using permeagraph and produce saturation magnetization of 0.6, 0.56, 0.42, and 1.00, remanent of 0.15, 0.19, 0.26, and 0.25, and coercivitas field of 0.35, 0.39, 3.0, and 1.29 kOe for composition of 0, 0.33, 0.67, and 1, respectively. The remanent magnetization ratio toward saturation of Br/Bs of this increase significantly from 0.34 to 0.62 for the composition x= 0.67, and has the highest energy produc of 0.195 MGOe. To determine the effect of Dy substitution towards micro structure was observed with an optical microscope. It was concluded that the effect of Dy substitution towards optimum magnetic behavior was found in the composition x= 0.67.

1. Introduction
Neodymium metal (Nd) was one of rare earth metals which has antiferromagnetic behavior, it means that this metal can be magnetized to become a magnet, but this metal has a Curie temperature which is the temperature at which the ferromagnetism disappears at 19 K (254 °C) [1, 2], so inside pure metal form, this Nd will be ferromagnetic only appear at very low temperatures. However, if this neodymium is combined with transition metals of iron and boron in certain compositions, a permanent magnet will be obtained that have a Curie temperature above room temperature and it’s known as neodymium magnet (Neo magnet).

Neodymium magnets was permanent magnets made from a mixture of neodymium, iron and boron for used a tetragonal crystal structure Nd$_2$Fe$_{14}$B [3]. Neodymium magnets was including strong rare earth magnets and are most widely used for several applications [4, 5]. Nd$_2$Fe$_{14}$B has been used to replace other types of magnets such as SmCo in more used as a component in industrial and high-tech products variation that require strong permanent magnets for several applications in the fields of electronics, automotive, telecommunications and transportation [1]. However, this Nd$_2$Fe$_{14}$B has many disadvantages including the most important is corrosion resistance and the operating temperature is
still low [2]. One way to overcome this is to substitute it with dysprosium (Dy). Dysprosium is considered to have the ability to increase the energy of anisotropy material, resistant to corrosion and can increase its operating temperature. Dy was substituted to the Nd site in an alloy of permanent magnet Nd$_2$Fe$_{14}$B [5, 6]. The amount substitution of Dy content depends on the application and for high-temperature applications such as wind turbine technology and motorcycle of Dy is large relatively.

The manufacture technology permanent magnet on Nd$_2$Fe$_{14}$B has been very established especially in developed countries [6-9], so the production of NdFeB permanent magnet materials was dominated by them; even the development of the technology has reached the nanoparticle and nano composite [10-12]. While for developing countries the technology of making permanent magnets is still difficult because it is constrained by the limitations of equipment facilities and the dependence on imported raw materials. Given these limitations, a breakthrough is needed in the form of innovation research that will lead to the empowerment of local natural resources aimed at national independence, learn the technology of making or producing Nd$_2$Fe$_{14}$B permanent magnets with simple technology and low-cost until maximum results are obtained.

In the framework of efforts to lead to the independence of the nation then the concrete step is to try to study the process of making NdFeB permanent magnets with the facilities and technology they have. In this study an attempt was made to create and characterize the permanent magnet Nd$_2$Fe$_{14}$B substituted with Dy metal using conventional technology through the arc melting method. The success parameter from the results of this sample is Nd$_2$Fe$_{14}$ phase formation in the sample. This phase formation can be fundamentally learned about phase analysis and crystallographic structures using X-ray diffraction facilities and supported by spectroscopy facilities and their magnetic properties. So the purpose of this study in general is to study the manufacturing process and the fundamental phase formation as a result of making Nd$_2$Fe$_{14}$B samples through the arc melting method, while specifically wanting to know the relationship between phase analyses with Nd$_2$Fe$_{14}$B magnetic properties.

2. Material and method

Formation of Neodymium Iron Boron Nd$_2$Fe$_{14}$B alloys following Niques-Technology launched by Sagawa et al. [13] and next developed by Manaf [14]. The raw material was a high purity iron metals: dysprosium Dy (sigma-Aldrich, 99.99%), neodymium Nd (sigma-Aldrich, 99.99%), iron Fe (Sigma-Aldrich, 99.98%), and boron B (sigma-Aldrich, 99.99+ %). Neodymium Boron iron substituted with Dy metal (Nd$_2$$_x$Dy$_x$Fe$_{14}$B) with various variations in the composition $x$= 0.00, 0.33, 0.67, and 1.00. Composition is calculated based on the stoichiometric rules. Each ingredient composition was put into graphite crucibles (1.25 cm in diameter, 7 cm in length) and in an under environment, under 0.5 atm Ar used conventional technology. A frit was placed above the first material to act as an alter during the centrifugation process. The crucibles are then protected in quartz ampules under 1/3 atm in Argon gas. Stoichiometric calculations for variations Dy substitution was shown in Table 1.

| Composition, $x$ | Sample                  | Mass of raw material (gr) |
|-----------------|-------------------------|---------------------------|
|                 | Nd$_2$Fe$_{14}$B        | Nd  | Dy  | Fe  | B  |
| 0.00            | Nd$_2$Fe$_{14}$B        | 3.30| 0.00| 6.56| 0.132|
| 0.33            | Nd$_{1.67}$Dy$_{0.33}$Fe$_{14}$B | 2.73| 0.62| 6.52| 0.131|
| 0.67            | Nd$_{1.33}$Dy$_{0.67}$Fe$_{14}$B | 2.17| 1.22| 6.47| 0.130|
| 1.00            | NdDyFe$_{14}$B          | 1.62| 1.82| 6.43| 0.129|
The Nd$_{2-x}$Dy$_x$Fe$_{14}$B samples that have been melted used an arc melting in the argon environment are then crushed the ingot and milled used high energy milling for 5 hours to obtain permanent magnet powder. The milling process used is high energy mill spex 8000.

Elemental composition analysis was carried out using electron microscope (MO) the Hitachi TM-3000. For all small crystal compositions crushed become powder and used to produce XRD patterns using PANalytical XPert Pro (Anode: CuKα, $\lambda = 1.54056 \text{ Å}$) with step size of 0.02°. The resulting peak the data or X-ray diffraction profiles were analyzed for lattice parameters using the Rietveld Method which is available with GSAS (general structure analysis system) software. While magnetic properties testing using the Permeagraph brand Physik 255 with a range of -2 to 2 tesla.

3. Results and discussions

The crystal structure of Nd$_2$Fe$_{14}$B has been determined to have a tetragonal structure (space group P 4 2/m mm, No. 136) in early 1995 by Isnard [5] listed in the open database crystallography (COD: 1008718). There are two separate and uneven Nd sites; one is a 4g site and the other is a 4f site. Also present are six unbalanced Fe sites and one unique B site. The qualitative X-ray diffraction (XRD) pattern using the Match program to identify the phases formed by the arc melting process. The identify result shows that all samples consisted of dominant Nd$_2$Fe$_{14}$B phase with tetragonal crystal symmetry and secondary phases were still found, namely Nd and Fe phases.

![Figure 1. X-ray diffraction pattern of the sample Nd$_{2-x}$Dy$_x$Fe$_{14}$B (x = 0 – 1) by using anode Cu-Kα.](image)

In the qualitative analysis uses the Match program, where the selection for phase identification refers to the possible phases that can be formed from raw materials Fe, Nd, and B. This program is equipped with the selection of elements in the periodic table so that it is able to detect possible phases which is formed based on crystallographic rules. Based on the results of qualitative analysis, it was found that the sample results from the synthesis consisted of 3 phases, namely the NdFeB, Nd and Fe phases.

Based on the results of the identification phase it appears that the arc melting process has succeeded in forming the dominant phase Nd$_{2-x}$Dy$_x$Fe$_{14}$B in the composition $x = 0 - 1$. It appears that in Figure 1 it is seen that the greater the Dy composition, the smaller the phase content, further analysis is needed to determine phase change, the amount of mass fraction formed and the effect of Dy substitution into the Nd atom. However, it should be noted that there is a correlation involving distance which has the
potential for a small anomaly to occur in the lattice parameter as a function of the presence of Dy substitution. This might be expected to change cell unit volume and atomic density as a Dy substitution function in Nd. This data can be obtained by refining X-ray diffraction patterns for each x composition.

In Figure 2 shows the results of refinement of X-ray diffraction patterns from the sample Nd$_2$$_x$Dy$_x$Fe$_{14}$B with variations in composition (x= 0 - 1). Figure 2 (a-d) is the result of refining the XRD pattern for x= 0 - 1 which has formed the Bragg diffraction peak with the dominant phase following the Nd$_2$Fe$_{14}$B structure. Quantitative analysis was carried out using the GSAS program and based on the results of the qualitative analysis of the Match program, the selected Crystallography Open Database (COD) was then collected in the form of a crystallography information file (cif) from the three phases to be used as input for the GSAS program. Qualitative and quantitative analysis refers to COD with card number (COD: 1008718), (COD: 5000217), and (COD: 180909) respectively for neodymium iron boron (Nd$_2$Fe$_{14}$B), iron (Fe), and neodymium (Nd) phases. The XRD data is then fitted with a pseudoVoigt model, a model that combines gaussian and lorentzian profiles. This model is very commonly used because it is considered the most suitable for fitting XRD patterns. The suitability parameter follows the Rietveld refinement method, which is based on the small R Bragg factor and Chi squared ($\chi^2$) whose value is close to 1 as shown in Table 2.

On the other hand, there was a noise and not a Bragg diffraction peak which was visible at an angle of 20=22°, because the peaks were not found in other compositions. So that this noise is considered negligible.

![Figure 2](image)

**Figure 2.** The result of XRD refinement of Nd$_2$$_x$Dy$_x$Fe$_{14}$B (x = 0 – 1) samples
A complete summary from the results of the improvement of X-ray diffraction patterns from the sample Nd$_{2-x}$Dy$_x$Fe$_{14}$B with variations in composition (x = 0 - 1) for all samples produced in Table 2. Figure 2 and Table 2 show that the results of the improvement of the X-ray diffraction pattern have the best fitting quality that can be obtained and the results are still within tolerance limits according to the fit (Rwp) and goodness of fit ($\chi^2$) criteria [18]. Rwp is the weight ratio of the difference between the observation pattern and the XRD calculation (Rwp ideal value <10%). Whereas $\chi^2$ (chi-squared) is the ratio from XRD result patterns to observations that were comparable to expectations.

Table 2. Structure parameter values, fit criteria (Rwp), goodness of fit ($\chi^2$) and phase mass fractions formed in the Nd$_{2-x}$Dy$_x$Fe$_{14}$B sample with variations in composition (x = 0 - 1).

| Sample  (x) | Phase   | Lattice parameter (Å) | V (Å$^3$) | $\rho$ (g/cm$^3$) | Fraction wt% | Rwp (%) | $\chi^2$ |
|------------|---------|------------------------|-----------|-----------------|--------------|--------|---------|
|            | Nd$_{2-x}$Dy$_x$Fe$_{14}$B | 8.8264(7) 8.8264(7) 12.269(1) | 955.8(2) 7.513 | 59.96          |              |        |         |
| 0.00       | Fe      | 2.8720(5) 2.8720(5) 2.8720(5) | 23.69(1) 7.829 | 39.21          | 32.37 2.81   |        |         |
|            | Nd      | 3.707(2) 3.707(2) 10.815(1) | 128.7(2) 11.163 | 0.83           |              |        |         |
| 0.33       | Nd$_{2-x}$Dy$_x$Fe$_{14}$B | 8.8233(4) 8.8233(4) 12.2455(8) | 953.3(1) 7.533 | 68.58          |              |        |         |
|            | Fe      | 2.8722(6) 2.8722(6) 2.8722(6) | 23.69(1) 7.827 | 30.54          | 27.91 1.86   |        |         |
|            | Nd      | 3.704(1) 3.704(1) 10.904(1) | 129.5(2) 11.115 | 0.88           |              |        |         |
| 0.67       | Nd$_{2-x}$Dy$_x$Fe$_{14}$B | 8.8151(2) 8.8151(2) 12.2111(5) | 948.88(8) 7.568 | 77.11          |              |        |         |
|            | Fe      | 2.8737(3) 2.8737(3) 2.8737(3) | 23.732(9) 7.815 | 22.65          | 20.62 1.45   |        |         |
|            | Nd      | 3.729(4) 3.729(4) 11.232(2) | 135.2(5) 10.621 | 0.24           |              |        |         |
| 1.00       | Nd$_{2-x}$Dy$_x$Fe$_{14}$B | 8.8187(3) 8.8187(3) 12.2278(6) | 950.9(1) 7.551 | 75.67          |              |        |         |
|            | Fe      | 2.8733(4) 2.8733(4) 2.8733(4) | 23.72(1) 7.818 | 22.76          | 20.13 1.44   |        |         |
|            | Nd      | 3.694(2) 3.694(2) 10.864(1) | 128.4(2) 11.191 | 1.57           |              |        |         |

The previous studies on the effects of substitution of rare earth metal elements on the Nd site have been carried out [15, 16] and included references in there. However, detailed quantitative experimental studies of the effects of Dy substitution with varying amounts in pure crystal samples have not been done much before. Pathek [17] studied these alloys to determine the crystal structure, magnetic anisotropy, and spin reorientation temperature in cerium substitution (Ce) with many inner variations in Nd$_2$Fe$_{14}$B achieved by varying the degree and type of substitution on rare earth metal sites (RE) and transition metal (TM). However, no detailed studies have been made regarding magnetic properties as a function of Dy’s concentration in this work. They also did not make a specific analysis of the stability of the compound (Nd$_{1-x}$Ce$_x$)$_2$Fe$_{14}$B. The maximum cerium substitution into Nd which can be achieved in the composition x = 0.38 (Nd$_{0.62}$Ce$_{0.38}$)$_2$Fe$_{14}$B.

In Figure 3 was a sample observation using an optical microscope and shows that the distribution of grain boundary from the composition x= 0 - 1 has a very good and uniform particle homogeneity across the surface of the sample with a relatively decreased grain diameter along with the addition of Dy metal. Figure 3 shows that the grain pattern of NdFeB is brownish white which is bordered by grain boundaries which are thought to have Fe deposits with a blackish brown color, and there is another impurity phase which is bluish white which is thought to be the Nd phase. In general, from the optical photo, the grain size appears wide in the range of 5-10 µm.
Figure 3. Particle morphology of \( \text{Nd}_{2-x}\text{Dy}_{x}\text{Fe}_{14}B \) which observed using MO a) \( x = 0.00 \); b) \( x = 0.33 \); c) \( x = 0.67 \); and d) \( x = 1.00 \).

In addition, the presence of Dy can be affected the magnetic properties of this system. In Figure 4, the results of the measurement of magnetic properties were shown using permeagraph. This test results a hysteresis curve which is the relationship between B magnetization and the external H magnetic. When the intensity of the H magnetic was increased to \( H = 1 \) Tesla, the B value experiences a saturation point called the saturation Bs magnetization. Next, the H magnetic field is lowered the curve of the curve does not return past the original curve. At the price of \( H = 0 \), B magnetization has a certain value. This condition is called Br remanent magnetization or material remanence. Then the price of the intensity of the magnetic field H is lowered continuously (negative value), the curve M will cut the axis in the magnetic field H which is denoted as Hc. It is this Hc intensity that is needed to make flux B= 0 or eliminate flux in the material. This magnetic intensity Hc is called material coercivity or coercivity field.
Figure 4. The hysteresis curve of Nd$_2$Dy$_x$Fe$_{14}$B

The saturation magnetization ($B_s$) for all samples was obtained from linear curve interception. All parameters specified ($B_s$, $B_r$, and $H_c$) were shown in Table 3. Remanent magnetization ($B_r$) and coercivity field ($H_c$) to the composition of $x$ (Dy concentration) in the sample Nd$_2$Dy$_x$Fe$_{14}$B was shown in Figure 5.

In the Figure 5 that the intrinsic coercivity of the magnet appears to increase significantly with increasing Dy concentration up to $x = 0.67$. Likewise, with remanence magnetization and maximum energy products increasing with increasing Dy until the composition $x = 0.67$. Furthermore, in the composition $x > 0.67$ both coercivity and remanent magnetization decreased. This is mainly due to the formation of phase Nd$_2$Fe$_{14}$B the greater the composition of $x = 0.67$, while the composition $x > 0.67$ phase decreases. This analysis is based on the results of refinement of X-ray diffraction patterns in the Figure 2.

Besides that, based on observations from the optical microscope in Figure 3 it appears that the presence of Dy is able to hold the growth of grain with optimum composition at $x = 0.67$ while for the composition of $x > 0.67$ part of Dy regardless of the composition of NdFeB phase. This result is also supported by changes in the volume of cell units that was getting smaller and the atomic density is enlarged at the optimum composition $x = 0.67$ (Table 2). So the optimum composition of $x = 0.67$ is obtained, the intrinsic coercivity value, remanent magnetization and energy products are the largest compared to other compositions.

4. Conclusion

A modified Nd$_2$Fe$_{14}$B based permanent magnet has been successfully made by substituting it with Dy metal using conventional methods of arc melting and mechanical milling. The Nd$_2$Dy$_x$Fe$_{14}$B alloy was made with several Dy concentration compositions of $x = 0.00, 0.33, 0.67$ and $1.00$. The identify result shows that all samples consisted of dominant Nd$_2$Fe$_{14}$B phase with tetragonal crystal symmetry and secondary phases were still found, namely Nd and Fe phases. Polish. The magnetic characteristic measured used Permeagraph produced saturation, remanent magnetization and coercivity fields that increased significantly in the composition $x = 0.67$ so that the composition of this was got the highest energy products was obtained to reach 0.195 MGOe. So the effect of Dy substitution can retain grain growth in NdFeB alloys and then it was increasing the energy anisotropy of ingredients.

5. References

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