The effect of FeMn and FeB additive on hematite ($\alpha$-Fe$_2$O$_3$) and their characterization

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Abstract. In this study, the mineral material addition of FeMn and FeB to the hematite ($\alpha$-Fe$_2$O$_3$) by varying each mass concentration of 0, 4, and 8 wt.% have been prepared by powder metallurgy method. The mixing process of the powder was done by high energy milling (HEM) for 1 h. Then, the powders were calcined at temperature of 1000 ºC for 2 h. The Effect of FeMn and FeB additives on $\alpha$-Fe$_2$O$_3$ causes the increasing of the particles diameter. The increasing of FeMn additive increases the powder density of material, but the addition of FeB decreases it. The material of $\alpha$-Fe$_2$O$_3$ with FeMn additive has dominant phases of $\alpha$-Fe$_2$O$_3$ and the minor phases of MnO$_2$ and Fe$_3$O$_4$. The material of $\alpha$-Fe$_2$O$_3$ with FeB additive has two phases as magnetite (Fe$_3$O$_4$) and hematite ($\alpha$-Fe$_2$O$_3$). The magnetic properties of a $\alpha$-Fe$_2$O$_3$ material with FeMn and FeB additives decrease the saturation value and coercivity.

1. Introduction

Material for magnetic is important because it is widely applied in the industries, including automotive. Indonesia has an abundant source of raw materials; one of them is iron sand. According to Widanarto [1] the form of iron sand that naturally occurs in mineral is ferrous ferrite (Fe$_3$O$_4$). By the heating processes at elevated temperatures, the resulting of magnetite phase (Fe$_3$O$_4$) changed into hematite ($\alpha$-Fe$_2$O$_3$) [2]. This change is followed by the changes in atomic arrangement and its magnetic properties [3]. Hematite ($\alpha$-Fe$_2$O$_3$) materials tend to stable at high temperature in comparison with magnetite (Fe$_3$O$_4$) [4]. Therefore hematite is more often used as a raw material for synthesizing ferrite magnets [5]. The ferrite magnet has strong mechanical properties, not easily corrode, high electromagnetic performance, excellent chemical stability, low coercivity, and moderate saturation magnetization [6, 7]. The hematite material ($\alpha$-Fe$_2$O$_3$) is an oxide that is widely used in various applications. Some applications are gas sensors, catalyst agents, lithium ion batteries [8], photoelectrochemical [9], biomedical devices, pigments, [10] and many others. Several methods are used for the preparation of $\alpha$-Fe$_2$O$_3$ such as sol gel, force hydrolysis, microemulsion, precipitation, direct oxidation, thermal decomposition, sonochemical, hydrothermal, solvothermal, and electrochemical [11, 12].
Ferro boron (FeB) is used as an additive for steel and iron because it can improve material mechanical properties and also the price is relatively cheap. Recently, FeB attract attention as a magnetic additive, one of which is the manufacture of NdFeB permanent magnets. FeB is a metal alloy composed of iron and boron with boron content ranging from 10 to 20%. Iron is widely used in the production of permanent magnets due to its high magnetic properties, while boron is hard and diamagnetic.

Ferro manganese (FeMn) has cubic structure and includes as soft magnetic. Manganese has a high melting temperature which is 1244°C, so it can retain at high temperature of such heat treatment. Therefore, the addition of FeMn into barium hexaferrite can decrease its magnetic properties.

In the previous study, Shen et al. [13] modified the nanocomposite Fe3O4-FeB and produced lower magnetic properties than Fe2O3. In other research, Lee [14] also synthesized Mn doped Fe2O3 and the magnetic properties decrease with increasing Mn. In this preliminary research, we apply FeM and FeB as doping to determine the properties within soft magnetic. FeM and FeB is applied due to have low magnetic properties. From this study, with addition of FeM and FeB into Fe2O3, it is expected to produce nanocomposite Fe3O4 with lower magnetic properties. The α-Fe2O3 is synthesized into pellet with the addition of iron manganese and iron boron (FeB) was carried out by powder metallurgy method and followed by the calcination process. Powder metallurgy is considered due to its easy and large scale applications.

2. Experimental Methods
FeMn and FeB additives were raw materials which were obtained from the nature with bulk form. Then, it was ground into powders to pass 200 mesh sieve. Furthermore, each of FeMn and FeB powders were added to the main raw material of α-Fe2O3 and milled using the high energy milling (HEM) shaker mill PPF-UG for 1 h. The variation of FeMn and FeB additives were 4 and 8 wt% which were added to hematite powder (α-Fe2O3). After milling, the powder was measured to find the powder density by pycnometer and its particle distribution was analyzed using the particle size analyzer (PSA). The powders were calcined at 1000°C for 2 h. Then the microstructure was analyzed by the X-ray diffraction (XRD - Rigaku SmartLab, Cu-κα 1.5406). While the magnetic properties were analyzed by using the vibrating sample magnetometer (VSM - Electromagnetic, 250).

3. Results and Discussion
The particle size distribution of α-Fe2O3 is shown in figure 1. While the distribution analysis and particle size of α-Fe2O3 after adding FeMn and FeB additives are shown in figure 2. From figure 2, it is clearly seen that the particle size differences based on the cumulative value diameter at statistical positions 10, 50, and 90%. The particle size distribution obtained is heterogeneous with the presence of peaks formed.

![Histogram](image)

**Figure 1.** Distribution histogram of mean particle diameter of α-Fe2O3.
Figure 2. Distribution histogram of mean particle diameter of (a) $\alpha$-Fe$_2$O$_3$ + 4% FeMn, (b) $\alpha$-Fe$_2$O$_3$ + 8% FeMn, (c) $\alpha$-Fe$_2$O$_3$ + 4% FeB, and (d) $\alpha$-Fe$_2$O$_3$ + 8% FeB.

Figure 3. The Correlation of powder density and mean diameter of hematite ($\alpha$-Fe$_2$O$_3$) with an addition of (a) FeMn, and (b) FeB.

The correlation between powder density and mean diameter of $\alpha$-Fe$_2$O$_3$ after adding FeMn and FeB are shown in figure 3. From figure 3, it can be seen that the effect of the addition of FeMn and FeB causing the mean diameter of particle tends to increase. It means that the milling effect for 1 h with high energy milling (HEM) has not been able to reduce the particle size of additives, where $\alpha$-Fe$_2$O$_3$ particle is around 1.7 µm. The powder density values tend to decrease with the addition of FeB additive, while the powder density tends to increase with the addition of FeMn additives.

Thus, it can be seen that the correlation between the powder densities to the mean diameter of FeMn addition is proportional, but inversely proportional for the addition of FeB. The density value of
FeMn, FeB, and α-Fe2O3 is about 7.3, 4, and 5.27 g/cm³, respectively. From those density values, the FeMn is higher than α-Fe2O3. Thus, density of sample increases with more addition of FeMn. Conversely, the powder density tends to decrease with the addition of FeB. The higher density of FeMn doped α-Fe2O3 than FeB doped α-Fe2O3 can be explained due to the hardness value of FeMn is higher than FeB. From this result, the number of density is strongly influenced by the heat treatment and material composition.

The phase analysis by using XRD of hematite powder (α-Fe2O3) after added by the FeMn and FeB are shown in figure 4. The obtained diffraction pattern are for (a) α-Fe2O3, FeB, and FeMn as raw material, and (b) the mixing of 4% FeMn + α-Fe2O3 and the mixing of 8% FeB + α-Fe2O3 additive after calcination at 1000°C for 2 h.

From figure 4 (a) the XRD analysis result of FeMn material shows the major peaks of FeMn phase. FeMn has a cubic structures and lattice parameters of \( a = 3.668 \) Å. In the diffraction pattern of FeB, it has single phases with lattice parameter of \( a = 4.053 \) Å, \( b = 5.495 \) Å, and \( c = 2.946 \) Å. While diffraction pattern of the α-Fe2O3 has a single phase which has a rhombohedral structure with lattice parameters of \( a = b = 5.032 \) Å and \( c = 13.733 \) Å. The diffraction pattern in figure 4 (b) is the diffraction of 4% FeMn + α-Fe2O3 and 8% FeB + α-Fe2O3. The obtained diffraction pattern shows three phases, which has α-Fe2O3 as the dominant phase and the two others phases are MnO2 and Fe(BO3)O phases.

![Figure 4](image)

Figure 4. X-ray diffraction pattern of raw materials (a) FeMn, FeB, and α-Fe2O3 and (b) α-Fe2O3 added 4% FeMn and 8% FeB with calcination at 1000 °C for 2 h.

The magnetic properties of α-Fe2O3 with an additive variation of FeMn and FeB before and after calcination is shown in figure 5. In table 1, it can be seen that the value of saturation, remanence magnetization, and coercivity of α-Fe2O3 are 0.68 emu/g, 0.12 emu/g, and 372.31 Oe, respectively. These values are low because the basic properties of the α-Fe2O3 material at room temperature are antiferromagnetic [15], so that this material will have very little response to the magnetic field. While for samples with 4 and 8% FeMn addition, it shown that the value of saturation, remanence magnetization, and coercivity are close resemblance as shown in figure 5 (a). These values are much greater than the value of the α-Fe2O3 material, but for sample with 4 and 8% FeMn addition after calcination at 1000°C for 2 h, its magnetic properties decrease to a quite low value as shown in figure 5 (b). This can be explained due to the addition of FeMn resulting the MnO2 phase as can be seen from the XRD results. Although the dominant phase in the sample is α-Fe2O3 which has antiferromagnetic properties, the appearance of MnO2 affects significantly its magnetic properties. The magnetic properties of a material are also influenced by other factors such as the degree of crystallinity, particle size and the presence of secondary phase effects [16]. Furthermore, the same phenomena shown on the sample with the addition of 4 and 8% of FeB followed by the calcination at 1000°C for 2 h. It is also found that due to the addition of FeB, it also forms the new phase of Fe3(BO3) (figure 2 (b)) that decreases the magnetic properties. From the result, prior to calcination, magnetic properties of each
sample is influenced by Fe$_3$O$_4$ and the additive, but after the calcination nanocomposite Fe$_2$O$_3$-FeMn produced MnO$_2$ and nanocomposite Fe$_2$O$_3$-FeB produced Fe$_2$(BO$_3$). Both Fe$_2$(BO$_3$) and MnO$_2$ have antiferromagnetic behavior, therefore their magnetic properties decrease.

![Graphs showing magnetic properties of α-Fe$_2$O$_3$ with additive variations of FeMn and FeB.](image)

**Figure 5.** Magnetic properties of α-Fe$_2$O$_3$ with additive variations of FeMn: (a) before and (b) after calcinations; and variations of FeB: (c) before and (d) after calcinations.

| Composition of FeMn (wt.%) | Before Calcination | After Calcination |
|---------------------------|--------------------|-------------------|
|                           | $\sigma_s$ (emu/g) | $\sigma_r$ (emu/g) | $jH_c$ (Oe) | $\Sigma_r$ (emu/g) | $jH_c$ (Oe) |
| 0                         | 0.68               | 0.12              | 372.31       | 19.76              | 10.31        | 1430.96        |
| 4                         | 1.09               | 0.18              | 352.04       | 1.55               | 0.48         | 380.98         |
| 8                         | 1.02               | 0.17              | 330.94       | 1.45               | 0.54         | 312.91         |

| Composition of FeB (wt.%) | Before Calcination | After Calcination |
|---------------------------|--------------------|-------------------|
|                           | $\sigma_s$ (emu/g) | $\sigma_r$ (emu/g) | $jH_c$ (Oe) | $\Sigma_r$ (emu/g) | $jH_c$ (Oe) |
| 0                         | 0.68               | 0.12              | 372.31       | 19.76              | 10.31        | 1430.96        |
| 4                         | 2.32               | 0.29              | 293.92       | 0.38               | 0.08         | 1326.18        |
| 8                         | 4.87               | 0.48              | 288.50       | 0.42               | 0.12         | 1350.24        |

**Table 1.** Magnetic properties of α-Fe$_2$O$_3$ with additive variations of FeMn, before and after calcined at 1000°C for 2 h.

**Table 2.** Magnetic properties of α-Fe$_2$O$_3$ with an additive variation of FeB, before and after calcined at 1000°C for 2 h.

4. Conclusions

Powder hematite (α-Fe$_2$O$_3$) with the addition of FeMn and FeB additives derived from natural raw materials has been successfully made with powder metallurgy method. Then samples were calcinated at the temperature of 1000°C for 2 hours. The analysis showed that the powder with the Fe$_3$Mn$_7$ addition has a dominant phase α-Fe$_2$O$_3$ and two new phases of MnO$_2$ and Fe$_3$O$_4$. The result of powder
density measurement showed that the optimum value was obtained for α-Fe$_2$O$_3$ sample with 8% wt Fe$_3$Mn addition. This material is classified as a hard magnet with magnetization value of saturation, remanent and coercivity of 24.0 emu/g, 10.3 emu/g and 571.8 Oe. The effect of 8 wt.% FeB addition on hematite (α-Fe$_2$O$_3$) material before calcination resulting the decrease of the coercivity value from 372.19 Oe to 285.06 Oe. The influence of calcination temperature 1000 °C for 2 h causes increasing of the grain growth and magnetic properties. While the effect of FeB addition at 0, 4, and 8 wt.% after calcination tends to convert the sample into soft magnetic with coercivity values of 1450, 1220 and 1180 Oe

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