Moderate thermal oxidation of iron oxide found in nature as raw materials for ferrite magnets

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Abstract. Iron oxide found in nature with high iron oxide content has potential to be utilized as raw material for magnetic application. In this study, an attempt has been made to increase hematite content through thermal oxidation or roasting in moderate temperature with additional oxygen gas to accommodate oxidation. Iron oxide powders were milled in 6 hours then washed and dried. Roasting processes were performed at four varying temperatures of 480°C, 520°C, 560°C, and 600°C with oxygen influx 3 L min⁻¹, preceded by isothermal holding at 385°C. TGA-DSC (thermogravimetric analysis – differential scanning calorimetry) and XRD (X-Ray Diffraction) characterization has been performed to understand iron oxide behavior in response to thermal oxidation at moderate temperature. It is observed that two main reactions are clearly distinguished. In DTG curve, first peak indicate reduction followed by oxidation at the second peak. XRD results has shown that the highest content of α Fe₂O₃ was achieved by roasting at 600 °C for 1 hour which produced hematite portion of 31 wt. %, yet it is still insufficient to be utilized as raw material for ferrite based magnets fabrication. To prevent reduction reaction of Fe₃O₄ which will retard the oxidation process, it is suggested to avoid isothermal run or lower heating rate at temperature below 406°C

1. Introduction
Ferrite magnets belong to ceramic magnets with chemical formula MO.Fe₂O₃. Ferrite magnets are highly utilized in electronics applications such as transformer core, digital data storage, signal transfer, circulator and DC motor[1-3]. Different M has different spin magnetic moment and likely alter crystal structure. Therefore, by adjusting composition and phases, it is possible to tailor their magnetic properties [2,4]. Co addition in ferrite magnets produces hard magnets with high coercivity, while Mn and Zn addition produces soft magnet with chemical formula Mnₓ(1-x)ZnₓFe₂O₄ [5,6].

Hematite or αFe₂O₃ has hexagonal or rhombohedral unit cell that is isostructural with corundum (αAl₂O₃). At room temperature it is weakly ferromagnetic, and at 260 K, it undergoes a phase transition to an antiferromagnetic state [7]. Magnetite and wustite are other forms of iron oxide, magnetite has Fe bivalent and trivalent atom and has spinel crystal structure. Magnetite is ferrimagnetic while wustite is paramagnetic at room temperature [8].

Standard ceramic method which involvement sintering process is widely used in ferrite magnets fabrication because it suitable for mass production. Fabrication of ferrite magnets use hematite or αFe₂O₃ as main raw materials. On previous research [9], barium ferrite magnets was fabricated through ceramic sintering method using iron oxide found in nature, resulted in 350 Gauss of intrinsic remanent induction. Further efforts to increase hematite content are required to enhance its magnetic properties. One way to achieve this is through thermal oxidation that allow Fe with lower oxidation number to be oxidized by oxygen gas. The purpose of this research is to study the response of iron...
oxide found in nature to moderate thermal oxidation and to measure hematite content achieved by this method.

2. Materials and Methods
Increasing hematite content from magnetite-dominant raw material was carried out by employing thermal oxidation method through roasting process. Powder of iron oxide found in nature was washed with water then dried, separated from dirt through magnetic separation method. Sample of 52.52% Fe content is examined by EDX characterization with remaining composition of 29.76% of O and minute content of Al, Si, Ti, and V. TGA-DSC characterization was performed to measure the mass change during heating. Iron oxide powders was milled using ball mill for 6 hour then proceeded with roasting. Heating started at room temperature then raised 10°C/minute, held at 385°C for 30 minutes, continued with heating at 10°C/minute, then maintained at four temperature variation for one hour, which were 480°C, 520°C, 560°C, and 600°C. Oxygen gas influx was added to accommodate oxidation in closed chamber with flow rate of 3L/minutes. XRD characterization was employed to determine phase composition ratio of initial powder and oxidation product and Rietveld refinement for quantification analysis.

3. Results and Discussion

Figure 1 shows TG (mass change) and DTG (rate of mass change) versus temperature at heating rate of 10°C /min. It can be seen that TG curve has nearly symmetrical curve, where mass-losing reaction occursand peaked at 406°C then the powders start to gain mass. These two processes of losing and gaining mass indicate there are two reactions take place. DTG curve refers to rate of change of mass per minute, where peaks show higher mass change per minute than flat ones. It demonstrates that peaks of DTG are related to the kinetics of reactions. From the DTG curve, the first reaction is peaked at around 330°C and second reaction is peaked at 507°C. After 507°C, mass change continueus progress with lower rate. However, the mass changes versus temperature curve are heavily influenced by the heating rate used during measurement, as study done by Lysenko et al.[10].From the Arrhenius equation, we can infer that the rate of reaction is influenced by Arrhenius parameter, activation energy, and temperature. To generate these data, it is suggested to use model-free method from TG curve with different heating rate as recommended by Vyazovkin and Wight [11].
Figure 2. TG and Heatflow of at heating rate of 10°C/minute

Figure 2 depicts DTG and HF (heatflow) versus temperature at heating rate of 10°C/min from room temperature to 800°C. We can see that the endothermic peak for first reaction is rather flat and exothermic peak at 494°C corresponds to DTG peak at 507°C. The exothermic peak is followed by less exothermic curve, and after 648°C, the reaction is gradually increasing exothermically with slight change in rate of mass change.

Figure 3. XRD patterns of different isothermal temperature of roasting process for 1 hour.

Figure 3 shows the XRD reflection intensity of initial powders and roasted powders with different isothermal temperatures. The initial powders constitute of Fe$_3$O$_4$, albeit the elemental composition of iron oxide found in nature reveals that there are other metals present such as Al, Si, Ti, and V. These metals have a low concentration thus their reflection intensity is much smaller than that of Fe$_3$O$_4$ and therefore it is entirely buried in the background noise. Isothermal run at 480°C shows peaks of FeO emerging. It demonstrates that a reduction reaction has occurred, in which the $\text{Fe}_3\text{O}_4 \rightarrow 3\text{FeO} + \frac{1}{2}\text{O}_2$ reaction has possibly taken place. This finding seems to be in agreement with the appearance of the endothermic peak in the HF curve, however, the temperature of the isothermal run is not in good agreement with DTG curve. According to DTG curve, at 480°C, mass-gaining reaction which indicate oxidation process should occur, yet XRD curve shows that reduction process has converted some
Fe$_3$O$_4$ to FeO. Results of quantitative analysis employing the Rietveld analysis code as shown in Table 1 indicate that 37.6 wt. % of Fe$_3$O$_4$ has been reduced to FeO, and parts of it were also oxidized to Fe$_2$O$_3$.

| Isothermal Temperature | Phases (wt %) |
|------------------------|---------------|
|                        | FeO | Fe$_3$O$_4$ | Fe$_2$O$_3$ |
| Initial Powders        | -   | 100         | 0           |
| 480°C                  | 37.6| 61.6        | 0.8         |
| 520°C                  | -   | 88          | 12          |
| 560°C                  | -   | 91          | 9           |
| 600°C                  | -   | 69          | 31          |

Isothermal run and non-isothermal run may have different kinetic parameters since they have different heating rates. It is also influenced by the pre-isothermal run at 385°C that according to DTG has reduced some Fe$_3$O$_4$ into FeO, thus alters kinetics parameter and differs from DTG curve. Furthermore, to prevent reduction reaction of Fe$_3$O$_4$ which will retard the oxidation process, it is suggested to avoid isothermal run lower than 406°C. Low heating rate also provide sufficient time to reduce larger amount of Fe$_3$O$_4$ into FeO.

Hematite formed during isothermal 560°C shows a slight decrease compared to roasting at 520°C, then shows a significant increase in 600°C isothermal. The isothermal run at 600°C produces the largest ratio of hematite at 31 wt. % compared to other isothermal temperatures. However, the ratio of hematite formed during roasting process is still insufficient to be utilized as raw materials for magnets fabrication.

### 4. Conclusion

During heating of iron oxide found in nature, it is observed that two main reactions are clearly distinguished. In DTG curve, first peak indicates reduction process followed by oxidation at the second peak. Pre-isothermal run at 385°C causes discrepancy between XRD and TGA-DSC results. XRD results have shown that the highest content of αFe$_2$O$_3$ was achieved by roasting at 600 °C for 1 hour which produced hematite portion of 31 wt. %, yet it is still insufficient to be utilized as raw material for ferrite based magnets fabrication. To prevent reduction reaction of Fe3O4 which will retard the oxidation process, it is suggested to avoid isothermal run or lower heating rate at temperature below 406°C.

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