Effect of Particle Size on Maximum Energy Product of Waste-derived Ferrites

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Abstract. Ferrite is an important component for electric motors, loud-speakers, EMI suppressors and transformer core. Hematite (Fe₂O₃) and strontium carbonate are commonly used to prepare ferrite. In this work, waste-derived hematite powder was milled using ball mill, high-energy milling and high-energy blender and the powder size was observed. The samples was further filtered according to different particle size, namely mesh 20, mesh 100 and mesh 400, and used as starting materials in the synthesis of strontium hard ferrites. Maximum energy product \( (BH)_{max} \) of the ferrites was analyzed by a B-H tracer. The results showed that the maximum energy product is significantly affected by particle size of the starting materials. As anticipated, the maximum energy product is inversely proportional to the particle size and the hard ferrite produced by high-energy blender obtained 0.99 MGOe. With that, it is confirmed that permanent magnets derived from waste materials is also affected by its particle size. Other magnetic properties such as remanence and coercivity are also reported in this paper.

1. Introduction

Hot rolling, i.e. processing a target metal above its recrystallization temperature, is a metal-working procedure that requires heating, rolling and forming of the target metal. Various steel products can be manufactured through hot forming, namely primary, section, flat, wire, rebar, profile, pipe and tube. These products can be generally categorized as long products. Billets or blooms are hot-rolled to produce such long products, of which are subjected to further rolling and drawing processes to form wire rods, tubes or coatings. Upon the completion of hot rolling, a layer of mill scale is formed on the surface of the steel due to reaction between the hot steel and atmospheric oxygen during the natural cooling process. Mill scale has a flaky appearance and consists of FeO, Fe₂O₃ and Fe₃O₄ [1]. Further processing of the steel (i.e. cold rolling) is preceded by the acid pickling process. Pickling liquor, a solution of strong acids such as HCL and H₂SO₄, is used as a cleaning agent to remove the mill scale layer from the surface. Alternative measures to clean the surface are electrolytic pickling and salt pickling. The scale-free steel is subsequently subjected to cold rolling below its recrystallization temperature to produce sheets and strips with superior surface finishing [2,3].
The setup of continuous acid pickling requires several tanks that serve different purposes. The hot-rolled steel is first submerged into tanks contained pickling liquor for to remove the mill scale layer. Subsequently, the steel is cleaned in water rinsing tanks to expel the pickling liquor. In Malaysia, spent pickling acid (SPL) is collected and recovered as recycled pickling liquor for further pickling operation or neutralized with low quality alkali to produce solid waste. The spray-roaster acid regeneration process and fluidized-bed process are the two main regeneration techniques utilized by the Malaysia steel industry players.

Strontium hard ferrite (SrFe$_{12}$O$_{19}$) used in this work is synthesized by utilizing waste products collected from local cold rolling steel factory. The waste products are subjected to milling, magnetic separation and heat treatment to produce hematite (Fe$_2$O$_3$). Hematite is then further processed to prepare strontium hard ferrite (SrFe$_{12}$O$_{19}$).

Iron oxide and strontium oxide are used to produce hard ferrite magnet. Mixing and pre-sintering of the raw materials (powder) are conducted to create the magnetic phase in the powder. Subsequently, the powder is subjected to pressing in an isotropic environment (absence of magnetic field). Finally, it is sintered to obtain the final product. From the market supply of magnets, hard ferrite magnets are the most economically competitive magnets due to the cheap cost of raw materials. Based on past literature, ferrites are determined to possess high electrical isolation effect and strong capability of resisting demagnetization in strong external magnetic fields [4-7]. High maximum energy product ($BH_{max}$), high residual induction (remanence) and high coercivity are crucial characteristics of a material to be capable of producing and maintaining its magnetic field [8, 9]. Materials in such category are termed oxide or ceramic magnets. The low cost of these materials contribute towards its wide usage in the market and industry. For the application of permanent hard magnet, the most commonly used material is hexagonal ferrite [10, 16].

In this work, the particle size of the oxide waste and the pre-formed powder was studied to confirm its effects on maximum energy product of the waste-derived hard ferrite.

2. Methodology
As aforementioned, waste products collected from local cold rolling steel factory were used as starting materials. Firstly, the waste products was divided into 3 samples and milled by using ball mill, high-energy milling (Model PM100) and high-energy blender (Model DM6), respectively. The milling period chosen was 24 h, 18 h and 10 minutes as suggested by the machine manufacturers. It was observed to be a useful process to reduce the size of large pieces into ultrafine powder. After drying and magnetic separation, heat treatment within the temperature range of 400°C to 600°C was executed on the powder. X-ray diffraction (XRD) analysis concluded that the Fe$_2$O$_3$ phase was present in all the samples. To segregate the powder according to different particle sizes, sieving was done with mesh 20, mesh 100 and mesh 400.

Strontium ferrite powder with magnetic phase was then produced by wet mixing and pre-sintering (at 1150°C) the Fe$_2$O$_3$ samples and strontium carbonate (SrCO$_3$) powder mixture, 6:1 was the selected mixing ratio of Fe$_2$O$_3$ to SrCO$_3$. The calcined samples were milled again via ball mill, high-energy milling and high-energy blending to produce single-domain particles. The 3 samples were sieved using mesh 20, mesh 100 and mesh 400 respectively before pelletized through pressing. The pellets were subjected to sintering for 7 hours at 1200°C. B-H tracer (Model Linkjoin MATS-2010H) was used to obtain the magnetic measurements of the pellets. Comparison of the maximum energy product, remanence and coercivity of the strontium hard ferrites was done. Figure 1 illustrates the procedure in synthesizing strontium hard ferrite sintered magnets.
3. Results and Discussion

Three different iron oxide layers can be observed in the waste products from the steel industry, namely wustite (FeO), magnetite (Fe₃O₄) and hematite (Fe₂O₃). The waste represents a rich source of iron due to its high iron (Fe) content of more than 70%. In this work, ultrafine single phase particles were obtained from the waste via milling. Defective FeO was collected via magnetic separation and oxidized into Fe₂O₃ that has more stability. The oxidation process is illustrated via Equation (1) [11]:

\[ 4\text{FeO} + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 \]  

(1)

X-ray diffraction analysis was employed to determine the presence of Fe₂O₃.

From Figure 2, the phase exhibited by the treated waste correlate to standard Fe₂O₃ phase, providing evidence that the Fe₂O₃ phase exists in the waste sample. On another spectrum, due to the absence of quantitative data of the sample from the XRD analysis, the purity of the Fe₂O₃ phase could not be determined.
To prepare strontium hard ferrite (SrFe₁₂O₁₉), the waste-derived Fe₂O₃ was subjected to the following the chemical reaction:

\[
\text{SrCO}_3 + 6\text{Fe}_2\text{O}_3 \rightarrow \text{SrFe}_{12}\text{O}_{19} + \text{CO}_2
\]  

The presence of SrFe₁₂O₁₉ phase was determined via X-ray diffraction analysis.
Figure 4: Hysteresis-graph of hard ferrite with Mesh 20 raw material.

Figure 5: Hysteresis-graph of hard ferrite with Mesh 100 raw material.

Figure 6: Hysteresis-graph of hard ferrite with Mesh 400 raw material.
The magnetic properties of the hard ferrite samples produced are illustrated by Figures 4-6. The column on the right displays the maximum energy product \((BH)_{\text{max}}\), remanence (B) and coercivity \((H_c)\) of the samples, whereas \(J/J_s\) is the squareness of the graph.

The highest maximum energy product is exhibited by mesh 400 sample at 0.990 MGOe, while mesh 20 and mesh 100 exhibit 0.260 MGOe and 0.750 MGOe, respectively. \((BH)_{\text{max}}\) defines magnet’s quality and amount of stored energy. On another spectrum, remanence represents the ability of a magnet to attract. Mesh 100 sample and mesh 400 sample have similar remanence at 1.943 kG and 1.941 kG respectively, indicating approximate equivalence in the samples’ attraction and repulsion abilities. In terms of coercivity, mesh 400 sample is rated at 5.321 kOe while mesh 100 sample is rated at 3.233 kOe. Such difference implies that mesh 400 sample has better resistance against demagnetization in an external magnetic field. In contrast, mesh 20 sample is determined to be a weak magnet due to its low remanence (1.619 kG) and coercivity (0.679 kOe) values.

According to the Stoner-Wohlfarth model, hard ferrite with good magnetic characteristics should satisfy the single-domain-particle concept [12-14]. In a single-domain magnet, its magnetization is oriented uniformly in one direction. However, in a multi-domain magnet (commonly larger samples), domain walls segregate the magnetic domains, creating a different direction of magnetization in each domain. Transition from domain to domain requires the magnetization to rotate according to the direction in the next domain. Such characteristics allow the multi-domain magnet to minimize the magnetostatic energy or internal energy of the magnet. When it is subjected to demagnetization (i.e. process of minimizing magnetic moment), the multi-domain magnet that possesses minimal internal energy has lower coercivity or resistance towards randomized direction of magnetization. In contrast, the single-domain magnet has much higher magnetostatic energy. Its uniformly oriented magnetization has to be rotated entirely for it to be demagnetized, hence having larger coercivity or resistance towards demagnetization. As such, the aforementioned magnetic characteristics of mesh 20 sample imply that it is not a single-domain magnet; whereas the mesh 100 sample is determined to have moderate magnetic properties as certain particles are sufficiently small to act as single-domain magnet. The mesh 400 sample, with the smallest particle size, is determined to be a single-domain magnet (according to the Stoner-Wohlfarth model) due to its high maximum energy product, good attraction ability and high coercivity [15].

4. Conclusions
The X-ray diffraction analysis was essential in this work to determine the phase stability of the samples. The XRD traces of Fe₂O₃ obtained from cold-rolled factory waste products was found to correlate with the JCPDS standard Fe₂O₃ phases. Preparation procedure, i.e. magnetic separation and heat treatment, was proven effective in obtaining hematite, Fe₂O₃, from the waste products. In addition, the SrFe₁₂O₁₉ magnetic phase was observed in the samples, providing evidence that the selected ratio of 6:1 for Fe₂O₃ to SrCO₃ was suitable to produce strontium hard ferrite sintered magnets. The variable factor, namely different particle sizes (mesh 20, mesh 100 and mesh 400), is concluded to be influential in determining the magnetic properties of the samples. The mesh 20 sample was found not a single-domain, whereas the mesh 100 sample only partially satisfy the single-domain sample. Only the mesh 400 sample (smallest grain size in this work) satisfied the single-domain-particle concept, therefore having the highest maximum energy product. In a nutshell, high-energy blender is recommended in this work in order to produce single-domain-particle for the synthesis of ferrite materials.

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