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A Study of Mill Scale Derived Hematite Process for NiZn Ferrite as EMI Suppressor in Terms of Magnetic Properties

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Abstract: Mill scale iron waste from the steel industry can be extracted into useful hematite and produced into a NiZn ferrite as an EMI suppressor. The function of an EMI suppressor is to 'choke' the electromagnetic interference produced by almost all electronic equipment, electrical wiring, wireless networks, etc. The most widely used material is NiZn ferrite as it can work at high frequency. Some good characteristics of NiZn ferrite toroid core is low permeability and high loss, namely resistivity, Relative Loss Factor (RLF) impedance and coercivity. To help the environmental waste problems and reducing cost, hence the idea to convert mill scale from the steel industry waste into hematite (Fe_2O_3) which is the most important element in producing NiZn ferrite. Successful conversion of the mill scale into hematite was proven by X-Ray Diffraction (XRD) analysis by designing and fabricating a magnetic separator. The NiZn ferrites were prepared by solid state reaction technique. The 3 samples of different methods of hematite extraction were prepared. The ferrites were tested by XRD, Scanning Electron Microscopy (SEM), permeability, RLF and coercivity. The process of hematite conversion by running the HM sample through the magnetic separator followed by permanent magnet shows the best result. It was proven by the sample HM that has the best characteristics for an EMI suppressor such as low permeability (63.6), high RLF (1.23) and high coercivity (5.873 Oe).

Key words: Mill scale, hematite, NiZn ferrite, EMI suppressor, magnetic properties, permeability, RLF, coercivity

INTRODUCTION

Ferrites may be defined as magnetic materials composed of oxides containing ferric ions as the main constituent. An example of a natural occurring ferrite is magnetite or ferrous ferrite (Goldman, 1991). It has been known, since the ancient time and its weak permanent magnetism found application in the lodestone of the early navigators (Jaswal and Singh, 2014). Ferrites are ceramic materials, dark grey or black in appearance and very hard and brittle. A ferrite core is made by pressing a mixture of powders containing the constituent raw materials to obtain the required shape and then converting it into a ceramic component by sintering.

In the past 30 years with the exponential advancement of complex digital applications in electronic and communication devices there has been a pollution of conducted and radiated Electro Magnetic Interference (EMI) that threatens to disturb the operation of much sensitive electrical equipment (Stojanovic *et al*., 2008). EMI may refer to any unwanted electromagnetic radiation emitted and/or conducted from an electrical source. Any electronic device or electromagnetic instrument such as computers, household appliances, wireless networks, control/power systems, high frequency-generating instruments, mobile communications and digital systems are considered to be the main source of this radiation. EMI can be found in a very wide range of frequencies, from the lowest ones like MHz up to a few GHz. EMI prevention is in critical demand due to the interference of these digital devices and also the increasing sensitivity and importance of electronic devices (Hutagalung *et al*., 2012).

Hence, EMI shielding is researched and can be defined as the prevention of the propagation of electric and magnetic waves from one region to another by using conducting or magnetic materials. The shielding can be achieved by minimizing the signal passing through a system either by reflection of the wave or by absorption and dissipation of the radiation power inside the material (Thomassin *et al*., 2013). In order to suppress the EMI, development of ferrite composites which has seen improvement in electromagnetic absorption has been focused on by Ghasemi *et al*. (2008). Spinel ferrite is becoming one of the most popular for the following merits including the high magnetic moment, ease of synthesis and stable performance (Wang *et al*., 2015). The most widely used materials for EMI suppression applications are soft ferrites, mainly of the nickel-zinc variety. The NiZn ferrite material does not affect signals on the low operational frequencies while it blocks the inductive EMI on high frequencies.

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One of the most versatile and widely known magnetic materials for general use is NiZn ferrite (Yadoji *et al*., 2003). NiZn ferrites have many applications in both high and low frequency devices and play a useful role in many technological devices. It agrees with the previous study by El-Sayed whom classed NiZn ferrites as 'good all-around performer' because they cover a range of applications from low frequency to microwave and from low to high permeability. They are soft ferrites with spinel structure and have also been proven by Hajalilou *et al*. (2015) to be one of the most versatile ferrite components for general use.

The NiZn ferrites are usually prepared by the conventional Solid State Reaction Technique that involves high temperature sintering and pressing (Zahi *et al*., 2007). The 3 raw ingredients to produce NiZn ferrite by solid state reaction are iron (3) oxide (Fe_2O_3), Zinc Oxide (ZnO) and Nickel Oxide (NiO) that can easily be found in the market. The mixing process is usually done by wet ball milling in a steel or ceramic container. Some of the advantages of solid state reaction are no particular solvents needed which means no waste disposal issues can be carried out quite easily and can produce high yield.

Mill scale is one of the major type of waste from steel industries and there are about 14 million tons of mill scale iron waste generated globally from the international steel industry yearly (Cho and Lee, 2008). In Malaysia alone, approximately 850 thousand tons of mill scale is produced annually and they are usually dumped at the factory yard discarded as waste and causes environmental problems. Mill scale is the by-product of the hot rolling of steel forming process. During hot rolling of steel, iron oxides form on the surface of the metal as scales. The scale is accumulated as waste material in all steel companies. Mill scale is also suggested to be rich in iron source containing about 70% of Fe in general and mainly consists of magnetite (Fe_3O_4), defective wustite (FeO) and minor amount of hematite (Fe_2O_3).

With this knowledge, it is hoped that the mill scale iron waste can be reproduced into man-made resource if recycled. It is desired that the wustite can be derived into hematite, a major component of producing NiZn ferrite and help to make good use of the iron waste by reducing the depletion of earth's natural sources, reducing pollution produced by discharging untreated waste and to save energy indirectly (El-Hussiny *et al*., 2011). A few methods have been suggested by several studies to recover the metallic components from the mill scale waste but none have been brought into commercialization (Cho and Lee, 2008). Studies regarding mill scale conversion into hematite and subsequently NiZn ferrite has been scarce.

MATERIALS AND METHODS

A key element in producing NiZn ferrite is iron (3) oxide (Fe_2O_3) which can be extracted from mill scale iron waste. An amount of 500 g of mill scale from the steel industry iron waste were gathered. The mill scale was cleaned and then filled into a steel container for milling process. The main purpose of milling in this stage is to crush the mill scale and produce a homogeneous mixture of the initial material. Distilled water and steel balls were added inside the steel container as the mixing medium. The ingredients were then milled by performing wet ball milling for 24 h at a speed of 20 rpm. The homogeneous oxide mixture was then filtered and left overnight. The resulting mass was dried in an oven at 100°C for 2 h to vaporize excess moisture.

After the sample has been properly dried, it was crushed using ceramic pestle and mortar to make it into powder form. The mill scale powder is consisted of iron (2) oxide (FeO), iron (3) oxide (Fe_2O_3) and iron (2, 3) oxide, (Fe_3O_4). The sample powder obtained in the previous process was kept in an oven for half an hour until the temperature reaches 100°C. The sample will then be passed through a magnetic separator with one tesla of magnetic field where the non-magnetic particles (wustite) will be separated from the magnetic particles (magnetite). Magnetite (Fe_3O_4) was attracted to the inner wall of the magnetic force whereas FeO will fell of and collected as wustite.

Wustite, FeO obtained from the magnetic separation process is oxidized at 550°C for 10 h. During the oxidation process, wustite, FeO was converted into hematite, Fe_2O_3, tentatively according to the Eq. 1 (Table 1) :

$$4\,FeO + O_2 \rightarrow 2\,Fe_2O_3 \quad (1)$$

After oxidation, the sample was again crushed using pestle and mortar and scanned using X-Ray Diffraction (XRD) to confirm the formation of hematite, Fe_2O_3. The NiZn ferrite is produced by solid state reaction with the hematite derived from mill scale as iron (III) oxide, Fe_2O_3 combined with Zinc Oxide (ZnO) and Nickel Oxide (NiO). The NiZn ferrite sample preparation was based on the chemical (Eq. 2):

$$0.3(NiO)+0.7(ZnO)+(Fe_2O_3) \rightarrow Ni0.3\ Zn0.7\ Fe_2O_4 \quad (2)$$

The raw materials were calculated accurately according to the molecular mole fraction and weighed accordingly. They are mixed together inside a steel container with steel balls and distilled water added as the

Table 1: List of samples for the experiment

Samples	Description
HM	Hematite ferrite that was derived from mill scale, extracted using magnetic separator and permanent magnet
HS	Hematite ferrite that was derived from mill scale, extracted slowly using magnetic separator only
HF	Hematite ferrite that was derived from mill scale, extracted using magnetic separator only (powder released faster)

mixing medium. The powders were mixed by wet ball milling for 24 h to obtain a uniform distribution of the components so that the mixture is homogeneous and achieve a degree of uniformity. Once the mixed oxides had been properly dried, the samples were crushed with pestle and mortar to turn it into powder form. The powder is calcined at a temperature of 1000°C for 20 h in a box furnace in order to gain uniform heating.

A few drops of Poly Vinyl Alcohol (PVA) solution was added to the powder as a binder and zinc stearate applied to the steel die as lubricant. The powder is inserted into the die and moulded into a toroidal shape by impaction from hydraulic pressing. The final sintering process takes place inside a furnace at a temperature of 1200°C for 20 h and left overnight to avoid rapid cooling. The resultant is a hard, black toroidal NiZn ferrite core. The 3 samples prepared of HM, HS and HF were referred by the basic Eq. 2 of ferrite and described in Table 1.

RESULTS AND DISCUSSION

The XRD analysis were applied to the samples to confirm the formation of hematite (Fe_2O_3) from mill scale iron waste. Figure 1 shows the XRD pattern of the hematite samples.

It can be observed that the peak intensity of the graphs compared between HM, HS and HF are all located at the correct scanning angles. They are mostly visible at 25, 34, 36, 41, 50, 54, 63, 64 and 72°. The graph is compared to the standard XRD chart of hematite formation. With these similar traits portrayed, it is assumed that the mill scale that was collected from the steel industry waste has been properly extracted and transformed into useful hematite for the formation of NiZn ferrites.

The morphology of the sintered samples are shown in Fig. 2. Scanned Electron Microscopy (SEM) micrographs were taken to assess the grain boundaries and the number of pores for the samples. From Fig. 2, the average grain size and number of pores of the ferrites were measured as tabulated in Table 2. It shows an increasing trend of size which is HM (average grain size 4.578 μm), HS (average grain size 6.532 μm) and HF (average grain size 8.696 μm). In terms of the number of pores taken in 400 mm^2 area, the trend shows a decreasing value. They are HM (28 pores), HS (25 pores) and HF (22 pores).

Table 2: Microstructure, shrinkage and density for ferrites

Samples	Average grain size (μm)	No. of pores in 400 (μm)^2
HM	4.578	28
HS	6.532	25
HF	8.696	22

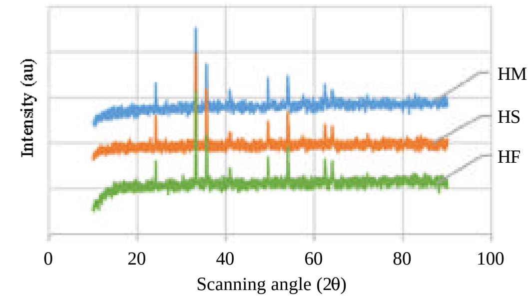

Fig. 1: XRD graph that shows the formation of hematite

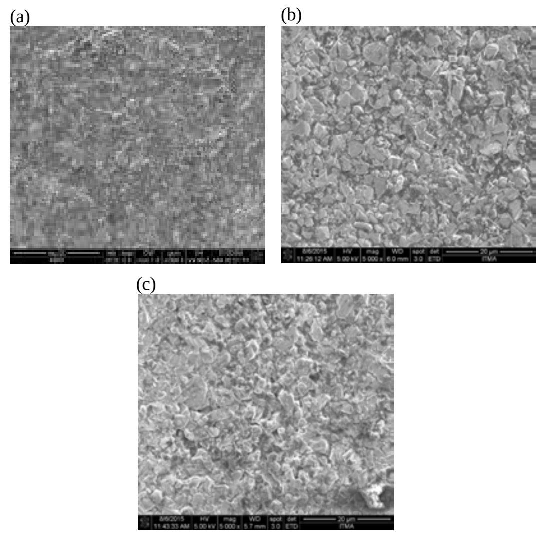

Fig. 2: SEM for mill scale ferrite samples: a) HM; b) HS and c) HF

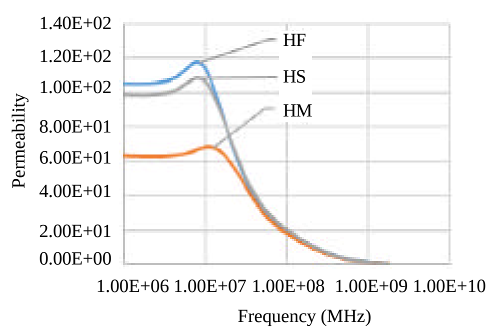

Fig. 3: Permeability vs. frequency graph for mill scale ferrite

In Fig. 3, the graph shows the permeability trend at the frequency of 1 MHz with the value for HM is 63.6, HS

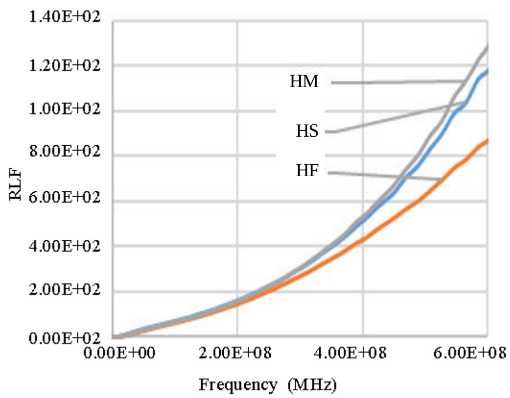

Fig. 4: RLF vs. frequency graph for mill scale ferrite

Table 3: Summary of magnetic properties

Samples	Magnetic properties	
	μ, f = 1 MHz	RLF, f = 600 MHz
HM	63.6	1.23
HS	98.5	1.14
HF	106.0	0.85

is 98.5 and HF 106. Here, HM is lowest compared to HS and HF, respectively. The permeability is low for HM because of its small grain size that contributes to the difficulty of domain wall movement. In accordance to this a high number of as shown in Table 2 is also a factor as it introduces a pinning effect that restricts the movement of the domain wall. Hence, permeability for HM is low compared to HS and HF that have a bigger grain size and less number of pores, respectively.

In Fig. 4, Relative Loss Factor (RLF) values at frequency 600 MHZ was presented for HM, HS and HF are 1.23, 1.14 and 0.85, respectively. It was clearly shown that HM has the highest loss followed by HS and HF. HM has the smallest grain size and highest number of pores as shown in Table 2 and this would evoke the domain wall motion much difficult. As grain size is small, there are more borders to get through it and as number of pores is high the pinning effect also take place and. More energy is needed to encounter these characteristics thus results in high.

In the Fig. 5, it portrays the hysteresis analysis for hematite ferrites. It features Here the coercivity (Hc) values of HM (5.873 Oe), HS (4.660 Oe) and HF (4.322 Oe). The value of HM is the highest because it has smaller grain size compared to HS and HF, thus it means more boundaries for the domain wall to move thru (Hajalilou *et al.*, 2015). The high number of pores also plays a factor here as more pores means pinning effect takes place and makes it difficult for the domain wall movement as it takes more energy (Table 3).

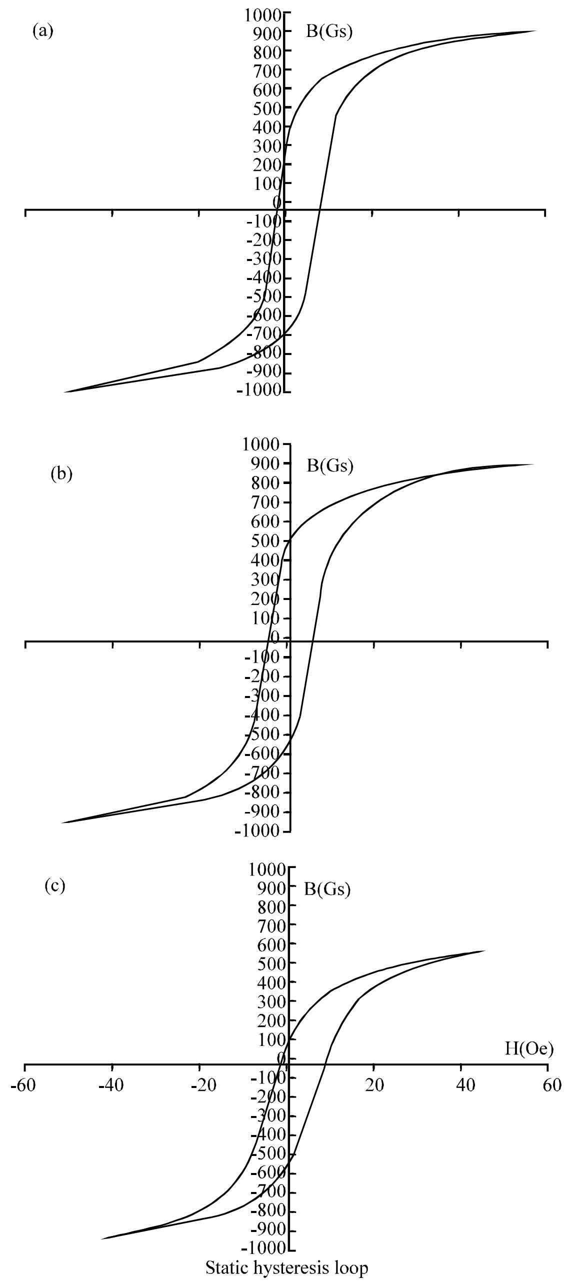

Fig. 5: Hysteresis graph for series A of mill scale ferrite; a) HM; b) HS and c) HF samples

CONCLUSION

The conversion process of mill scale iron waste into useful hematite by means of milling, magnetic separation and oxidation was proven successful from the XRD analysis. A NiZn ferrite for EMI suppressor can be fabricated by recycling the waste derived hematite. The best method to extract hematite is by passing through a magnetic separator and permanent magnet because of the high magnetic losses incurred. It was proven by the sample HM that has the best characteristics for an EMI suppressor such as high RLF, high coercivity and low permeability. The summary of results in terms of magnetic properties can be seen in Table 3.

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