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ANNEALING STUDY OF α-Fe_2O_3 NANOPARTICLES STEEL-WASTE BASED: MICROSTRUCTURE AND MAGNETIC BEHAVIOR

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ABSTRACT

The interest of this paper is to show the influence of annealing process on magnetic properties and microstructure of α-Fe_2O_3 derived from steel waste product (mill scales). The mill scales flakes were wet ball milling for several hours to form a fine powder. The mill scales powder was purified by using magnetic separation to isolate the magnetic and non magnetic particles. The method was continue for Curie temperature separation technique. The purified powder was annealed at 400/450/500 and 550 °C at 6 °C/mins to form hematite, α-Fe_2O_3. The annealed powders were milled for several hours by using mechanical alloying. Annealing at varied temperatures produced α–Fe_2O_3 nanopowders with average crystallite size 18.1 nm to 28.6 nm. Phase transformation occurred directly by annealing in air, conversion of FeO and Fe_3O_4 phase to form α-Fe_2O_3. The correlation between the magnetic properties and microstructure, of the sintered powders at 1200 °C enables to obtain microphase of α-Fe_2O_3 and Fe_3O_4 with different particle size and magnetic properties. The resultant α-Fe_2O_3 nanopowders are ferromagnetic with moderate coercivities.

Keywords: Fe_2O_3; steel waste; particle size; magnetic properties; mechanical alloying;

INTRODUCTION

Iron (III) oxide also called ferric oxide is the inorganic compound with symbol α-Fe_2O_3. It also known as hematite, the main source of iron for many steel industry. It is ferromagnetic material with dark red color. The crystallographic parameters of α-Fe_2O_3 is shown in Table 1. α-Fe_2O_3 is antiferromagnetic below −13.15 °C and exhibits weak ferromagnetism between −13.15 °C and the Néel temperature, 677 °C [1]. α-Fe_2O_3 magnetic properties are influence on many factors, such as particle size and magnetic field intensity. It has important properties, such as its magnetic and structural phase transitions of nanoparticles. The existence of amorphous Fe_2O_3 and four groups (α, β, γ,

and ε) is well established [2]. The α–Fe_2O_3 having a rhombohedral-hexagonal crystal system *R-3c* and cubic spinel structure γ–Fe_2O_3 (maghemite). At a temperature of 650 ^oC, hematite turns into Fe_3O_4 with a high energy loss.

Table 1: Details of α-Fe_2O_3 crystallographic parameters

Mineral:	*Hematite*
Chemical name:	*Alpha−Iron(III) Oxide*
Common name:	*Hematite*
Chemical formula:	*α–Fe_2O_3*
Crystal system:	*Hexagonal*
Space group:	*R−3 c*
Space group number:	*167*
b (Å):	*5.03*
c (Å):	*13.75*
Alpha (°):	*90.00*
Beta (°):	*90.00*
Gamma (°):	*120.00*
Calculated density (g/cm^3):	*5.27*
Measured density (g/cm^3):	*5.26*
Volume of cell (10^6 pm^3):	*301.67*

Iron oxide nanoparticles widely used as a catalyst and gas sensitive material [3]. Iron oxide nanocrystalline mostly used to enhance materials performance and improve industrial processing. For instance, the ferrites synthesis can be formed at lower temperature (900 ^oC) when using Fe_2O_3 nanopowder as a starting raw material [3][4]. Additionally, the gas sensitivity of α-Fe_2O_3 also can be improved remarkably by using the ultrafine α–Fe_2O_3 powders [3]. Therefore it is importance to control the particle size and morphology of the iron oxide. Varied methods has been used in preparing nanosized α–Fe_2O_3, such as the thermal decomposition of precursors [5], combustion method [6], thermolysis of PVA gels [7], used to controlled particle size and lower cost. There are two crystalline types of Fe_2O_3, i.e. maghemite (γ-Fe_2O_3) and hematite (α–Fe_2O_3). The phase transition of α-Fe_2O_3 takes place during calcination at 400 ^oC [3]. The phase transformation occurs during calcination transformed to α-Fe_2O_3 phase which undergone an aggregation and grain growth [8]. High energy mechanical process of solids has become extremely important in many processes such as chemical technology and materials science [8]. Many solid state reactions, which normally occur at elevated temperatures, can be facilitated by mechanical treatment. The steel waste, as well known a steel scrap or mill scales is a waste product from steel industries [8]. Steel waste is a form of flakes and grey in color, contains a mixture of silica, calcium oxide, magnesium oxide, and aluminium oxide and iron oxides. Steel waste also consists of iron oxide element, such as wustite (FeO), magnetite (Fe_3O_4), hematite (Fe_2O_3) along

with small amount impurities, such as carbon, barite, steel powders, metal shavings and steel punchings [9][10][11][12]. The purposes of this paper is to study the influence of heat treatment dependence of the magnetic properties and microstructure will be discussed.

METHODOLOGY

Sample preparation

The steel waste synthesis and purification of iron oxide to produce high purity Fe_2O_3 are referring to Azis et. al [8][9]. The steel waste making product was wet ball milling by using steel balls with 1 to 3 mm diameter at medium milling speed for several hours by conventional solid state mixing. The steel powder (150 μm) is filled in the tube with the deionized water with apply 1 Tesla magnetic field. The magnetic powder was then purified with the magnetic and non-magnetic particles (MNM) and Curie temperature separation (CTS). The powder is annealed at 400/450/500/550 ^oC in air for 6 ^oC/mins. 0.108 moles α–Fe_2O_3 were milled by using mechanical alloying (high energy ball mill (HEBM)) with the ratio of 10:1 for 6 hrs. The powder was then pressed at 40 kN using hydraulic pressing machine. The pallet sample with diameter 10 × 11 mm thickness is sintered at 1200 ^oC for 6 hours in air at 6 ^oC/mins.

Characterization

The phase structure of powder was observed by using XRD (Philips Expert PW3040 diffractometer). The measurement was carried out at room temperature, using diffraction angle (2θ) range of 10 to 80^o, with an increment of 0.1^o. The data was then analyzed by utilizing software X'pert HighScore and was compared to the electronic PDF2 library. The surface morphology is examined by using field emission scanning electron microscopy (FESEM) (FEI NOVA NanoSEM 230). The magnetic properties of samples are determined by its hysteresis using vibrating sample magnetometer (VSM) (Lake Shore 4700), maximum magnetic field of 15 kOe. The saturation magnetization (M_s), remnance magnetization (M_r), and coercivity (H_c), were recorded at room temperature VSM. The elemental analysis of powder were examine using Energy Dispersive Analyzers (EDX) EDX-720 and X-ray Flurosence (XRF) JED-2300. The diameter sizes of particles were determined by using average grain intercept (AGI) method.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of purified steel waste powder after annealed at 400/450/550 ^oC. The detail XRD parameter are tabulated in Table 1. The results show the purified steel waste powder annealed at 400/450/550 ^oC shows the phase transformation of purified steel waste powder to form hematite α–Fe_2O_3. The diffraction peaks match the ICSD Ref. No. 98-004-1069 which is a rhombohedral structure with space group *R–3c.* Increase annealing temperature at 550 ^oC, the hematite form with second phase magnetite Fe_3O_4. The diffraction peaks obtained correspond to

the phase of Fe_3O_4, ICSD Ref. No. 98-005-9302, which is a orthorhombic structure with space group *Imma*. The diffraction pattern at the (012), (110), (104), (110), (113), (202), (024) and (112) planes are belong to the α–Fe_2O_3 phase. The appearance of the Fe_3O_4 phase during reaction is a clear evidence that the valence change from Fe^{3+} to Fe^{2+} must occur due to the fact that Fe^{2+} ions occupy the octahedral sites of Fe_3O_4 [13]. Strong diffraction patterns at (112), (211), (004) and (105) are represent Fe_3O_4 phase. From Table 1, we can observed the influence on annealing temperature on the crystallite size. The estimate crystallite size of annealed powder are in range 18.1 nm to 28.6 nm. The crystallite size can be observed by the change of the full width of half maximum (FWHM) of the highest XRD peak. The diffraction peak width for powder annealed at 400 ^oC to 550 ^oC was decrease, as increase the crystallite size. Increase temperature to 500 ^oC, the peak width is getting narrow and reduce the peak width as increase the crystallinity. The hematite α–Fe_2O_3 was the only phase present for the powder heated below 550 ^oC.

Table 1: Details XRD parameters for powder annealed at varied annealing temperature in air

T (^oC)	Pos. (°2th.)	Height (cts.)	FWHM (°2th.)	*d*-spacing (Å)	Ref. Code	Crystallite size (nm)	Phase
400	35.5015	1607.19	0.5432	2.52659	98-004-1069	18.1	α–Fe_2O_3
450	35.5101	1479.20	0.5306	2.52600	98-004-1069	18.4	α–Fe_2O_3
500	33.1327	2558.42	0.2799	2.70161	98-004-1069	27.8	α–Fe_2O_3
550	35.5649	1944.01	0.1336	2.52223	98-004-1069 98-005-9302	28.6	α–Fe_2O_3 + Fe_3O_4

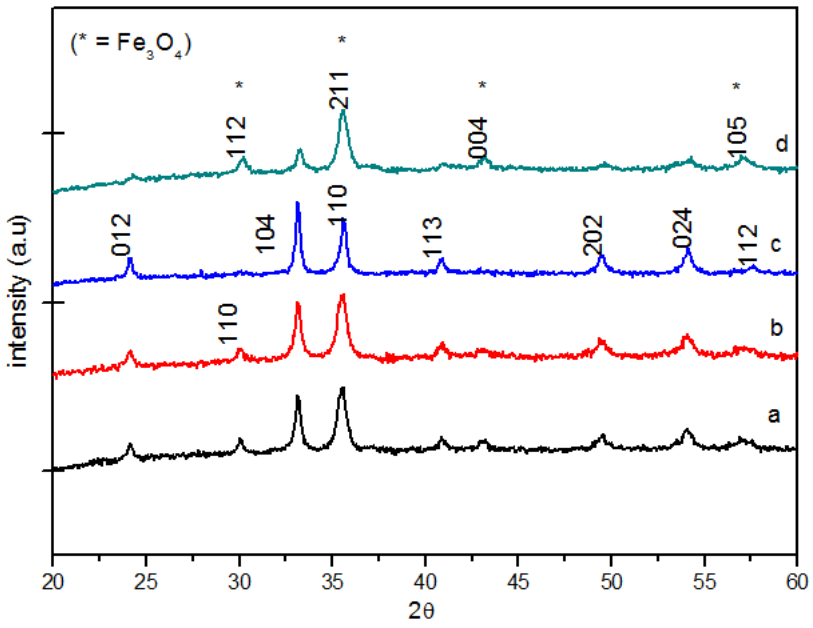

Figure 1: X-ray diffraction patterns of powder annelaed at (a) 400 ^oC (b) 450 ^oC (c) 500 ^oC (d) 550 ^oC

Figure 2 shows the % Fe content of the purified steel waste powder after heat treatment process. The graphs show the purification process yields high Fe content from the steel waste product ~ 98 %. The steel waste also contains small amount of impurities Mn, Cr, Cu and Ca ~ 2 %. Figure 3 shows the FESEM images of steel waste sample sintered at 1200 ^{o}C. It is apparent that the temperatures increase; the average grain size increases. The average grain size gives a value of (a) 4.73 µm, (b) 5.16 µm, (c) 5.24 µm and (d) 5.43 µm at 1200 ^{o}C (Figure 3). Grain size increases with temperature is sufficient to move grain boundaries and tend to agglomerate.

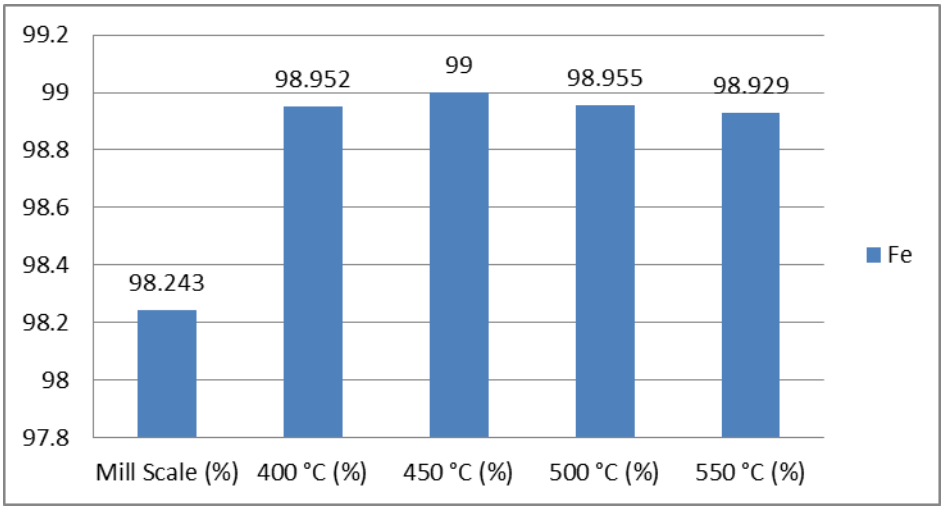

Figure 2: % Fe content produce after annealing process at varied annealing temperatures

The increase the annealing-sintered temperature shows a varied in the magnetic properties of α-Fe_2O_3. The saturation magnetization M_s and retentivity M_r for mill scales are 15.24 emu/g and 0.91 emu/g respectively. The M_s of α-Fe_2O_3 obtain are (a) 28.65 emu/g, (b) 21.77 emu/g , (c) 8.7569 emu/g and (d) 31.39 emu/g, respectively (Figure 4). The M_r obtain are 5.43 emu/g, 4.47 emu/g, 1.62 emu/g and 7.33 emu/g, respectively. The varied M_s is believed to result from change particle size and the crystal and shape anisotropy [7]. An increase in M_s is often observed with the increasing particle size which can be attributed to the surface contribution, surface defects, and stoichiometric deviation [7]. The coercivity H_c also change from 8.75 Oe to 31.39 Oe (Figure 5). The H_c of unheated mill scales obtain is 0.91 Oe. The samples shows an average grain size from 4.73 µm to 5.24 µm. The magnetic parameters anomalous attributed as a function of increase temperatures. This magnetic behavior may perhaps be attributed to the shape anisotropy effects and to the extensive agglomeration of the magnetic particles [7].

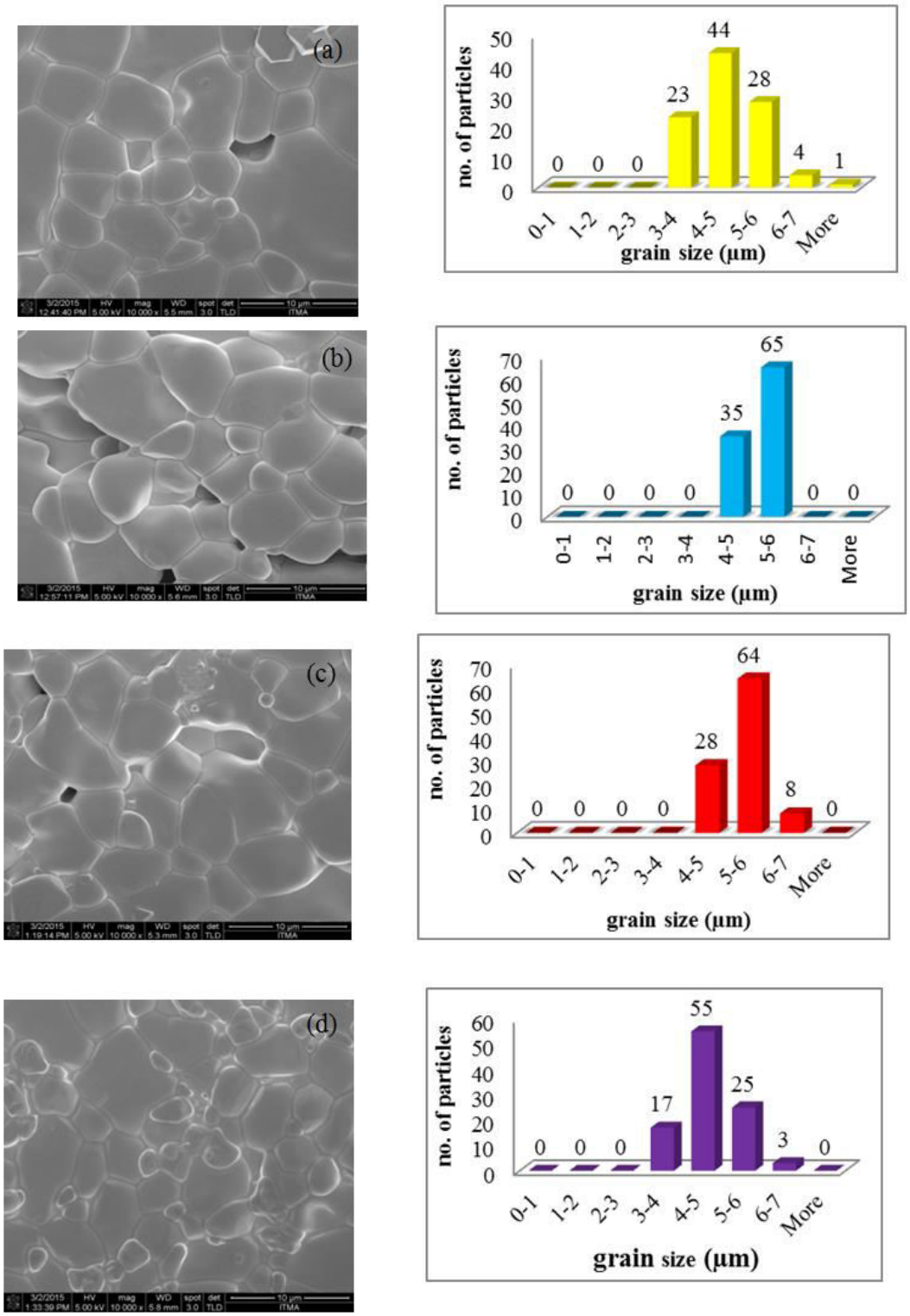

Figure 3: FESEM images and average grain size observed for Fe_2O_3 annealed at (a) 400 ^oC (b) 450 ^oC (c) 500 ^oC (d) 550 ^oC and sintered at 1200 ^oC

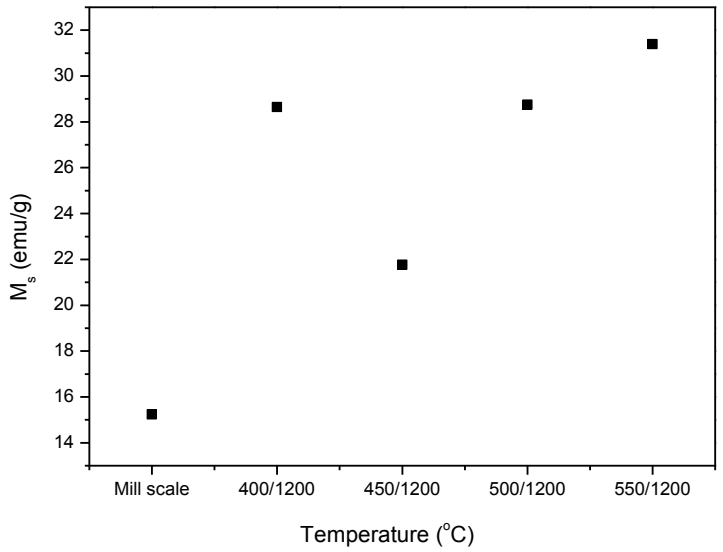

Figure 4 : Saturation magnetization M_s of samples at varied temperatures

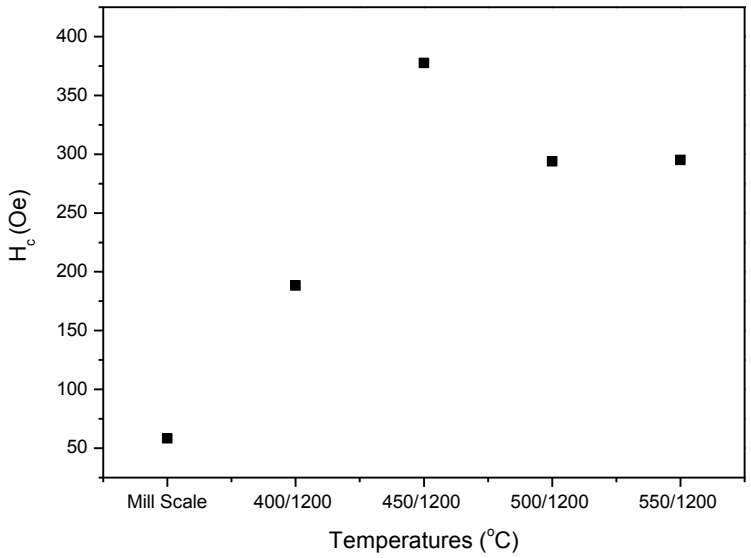

Figure 5 : Coercivity H_c of samples at varied temperatures

CONCLUSION

Nanocrystalline α–Fe_2O_3 oxides were prepared by using wet mixing–annealing process, steel waste based. The purified steel waste was annealed at varied temperatures 400/450/500/550 ^oC. Increase annealing temperature to 550 ^oC, the α–Fe_2O_3 occur a phase transformation to Fe_3O_4 phase. The high energy mechanical treatment of α–Fe_2O_3 powder enhanced microstructure development by preventing the development of pore structure, thus obtaining uniform, fine-grained microstructures after sintered at 1200 ^oC. As the sintered temperature increase, the coercivity H_c increases in response to the increase of average particle size. This results show the formation of high content of Fe_2O_3 below 570 ^oC, as previously reported. The iron oxide nanomaterials are ferromagnetic irrespective of their phase identity as well as hysteresis attributes.

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