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STRUCTURE AND MAGNETIC PROPERTIES OF FE/SI NANOPARTICLES PREPARED BY HIGH ENERGY MILLING PROCESS

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ABSTRACT

The structure and magnetic properties of Fe/Si nanoparticles prepared by the high energy milling process have been investigated in terms of the phase transition. Fe/Si nanoparticles were processed by high energy milling (HEM) for 10 hours to 50 hours with a weight per cent ratio of 9:1. Based on the X-ray diffraction (XRD) pattern, transmission electron microscope (TEM) observations, and vibrating sample magnetometer (VSM) analysis, the phase transition induced by HEM. The effect of structure and particle size on magnetic properties were also studied. It was found that iron and iron oxides (γ-Fe_2O_3/ Fe_3O_4) phase were exhibited on all milled samples. The magnetization value of Fe/Si nanoparticles increased up to 20 hours with 142 emu/gr saturated magnetization and then decreased linearly with increasing milling time. Referring to the XRD result, this decline was initially caused by the iron oxide formation and magnetic interaction between iron and iron oxides nanoparticles. The phase and magnetic properties value changes related to the interaction mechanism between Fe atoms caused by interstitial occupied of Si atoms, particle size reduction, and oxidation process.

Keywords: structure, magnetic, nanoparticle, milling

ABSTRAK

Struktur dan sifat magnetik nanopartikel Fe/Si yang dibuat dengan proses milling energi tinggi telah diperiksa, dengan fokus pada transisi fasa. Nanopartikel Fe/Si diproses dengan high energy milling (HEM) selama 10 jam sampai 50 jam dengan perbandingan persen berat 9:1. Berdasarkan pola difraksi sinar-X (XRD), pengamatan mikroskop elektron transmisi (TEM), dan analisis vibrating sample magnetometer (VSM), terbukti adanya transisi fasa yang diinduksi oleh HEM. Pengaruh keadaan struktural dan ukuran partikel pada sifat magnetik seperti magnetisasi juga dipelajari. Ditemukan bahwa fasa besi dan oksida besi (γ-Fe_2O_3 /Fe_3O_4) terlihat pada semua sampel yang digiling. Nilai magnetisasi nanopartikel Fe/Si meningkat hingga 20 jam dengan magnetisasi jenuh 142 emu/gr dan kemudian menurun secara linier dengan bertambahnya waktu milling. Mengacu pada hasil XRD, penurunan ini awalnya disebabkan oleh pembentukan oksida besi dan interaksi magnetik antara nanopartikel besi dan oksida besi. Perubahan nilai sifat fasa dan magnet berkaitan dengan mekanisme interaksi antar atom Fe yang disebabkan oleh adanya interstisial atom Si, reduksi ukuran partikel, dan proses oksidasi.

Kata kunci: struktur, magnetic, nanopartikel, milling

INTRODUCTION

Nanomaterials have unique electrical properties, chemical and magnetic structures. It is widely used in many fields, such as data storage, applications of biosensors, and biomedical engineering[1]. One type of well-developed nanomaterial is a magnetic nanomaterial. If the size of the magnetic particles is reduced to the nanometer scale, it showed different magnetic properties, such as ferromagnetic on the bulk system, into nanometer-sized superparamagnetic particles[2,3]. Soft magnetic materials with nano-sized structures improved magnetic properties when the grain size is less than the ferromagnetic[4,5]. Magnetic nanomaterials are magnetic nanoparticles based on oxides such as Fe and Fe_3O_4 (magnetite), γ-Fe2O3 (maghemite) and ferrite[6]. These materials have a strong magnetic response, such as lower permeability and higher coercivity than micron-sized particles[7], but it tends to be unstable on oxidation and thermal processes. Therefore, it is essential to modify the magnetic nanoparticles so that the nanoparticles are more stable to oxidation and thermal processes without reducing the magnetic properties significantly.

Magnetic nanoparticles of Fe-based oxide can be modified by forming nanocomposite with silica. Some research nanocomposite Fe/Si systems showed the formation of nanoparticles are stable in biological environments and high temperatures[8,9]. It has also been carried out a synthesis of Fe-SiO_2 nanoparticles by chemical co-precipitation technique[10], arc-discharge[11], and so-gel[12]. Several methods for preparing magnetic nanoparticle materials have been developed by physical technique[13-15].

The large size starting materials can be scaled down to nano-size by this technique, such as the high energy milling (HEM) method[16]. HEM is a process with a mutual collision between the balls and the powders (material) and a convenient technique to produce alloy powders from elemental powders. Non-equilibrium solid solution phases and nanocrystalline microstructures can be produced by this technique[17]. This process crushed powders into fragments. The milled powders are characterized based on the initial powders, milling speed, and time[18]. This process can be modified and added to another element to obtain higher material properties. The objective of this research is to study the influence of milling time on the structure and magnetic properties of nanoparticles of Fe/Si using the HEM technique in terms of particle size.

METHOD

Materials Fe (Sigma Aldrich, 97%, CAS# 7439-89-6) and Si (Sigma Aldrich, 99.998% 7440-21-3) powders were mixed with Fe: Si = 9:1 composition and a total weight of 10 grams. Powders mixture were milled with different milling times 10, 20, 30, 40 and 50 hours by SPEX CertiPrep 8000M Mixer/Mill at speed 1485 rpm in the argon atmosphere. The milling vial was sealed with a flexible O-ring to reduce oxidation. The milling process was stopped for 1.8 hours after every 5.4 hours of milling for cooling purposes. Powder samples were taken from the selected milling time for analysis and characterization.

The powder samples were observed by a JEOL 1200 transmission electron microscope (TEM) at 120 kV to obtain particle size and structure. It was also analyzed by Phillips PW1107 X-ray diffraction (XRD) equipment using CuKα radiation.

The peak position, half-maximum width, and material phase were obtained by the XRD (3rd generation Empyrean, Malvern Panalytical) measurements, and it was analyzed by the Hanawalt method. Magnetic parameters were measured by vibrating sample magnetometer (VSM), with a range of external magnetic field of ± 1 Tesla at room

temperature, gain acceleration and 0.25 Tesla per minute of reduction of the external magnetic field.

RESULTS AND DISCUSSION

A TEM bright-field image of a particle of Fe/Si powder after milling 10, 20, 30, 40 and 50 hours, as seen in Figures 1. The corresponding selected area diffraction pattern (SADP) pattern shows the body-centred cubic (BCC) α-Fe structure in all TEM micrographs. The spherical Fe and elongated Si powder were observed with a particle size of about 30 nm.

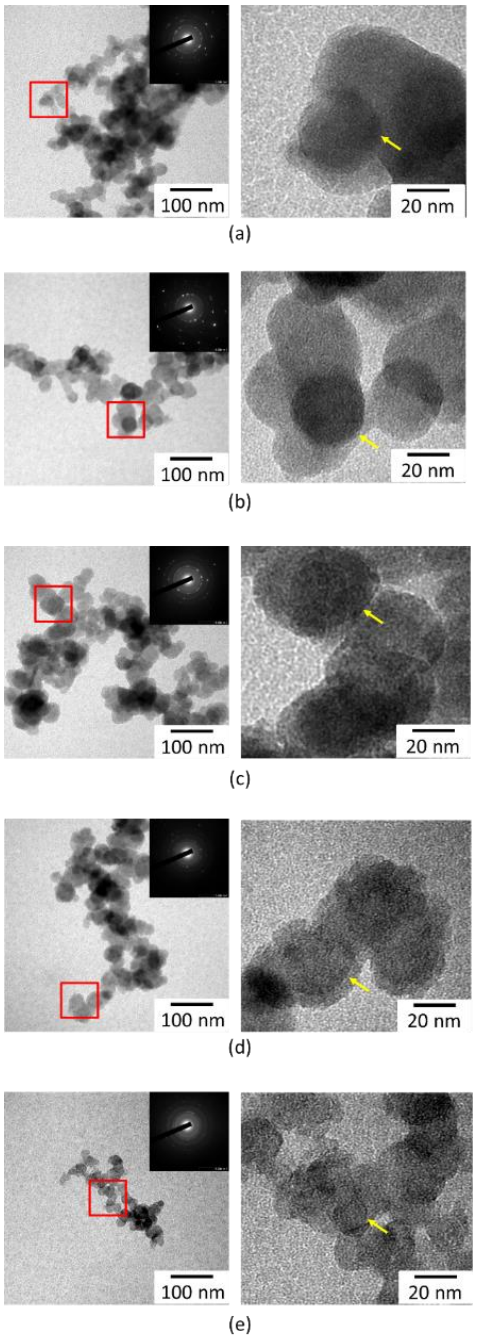

Figure 1. TEM micrograph for (a) 10 hours, (b) 20 hours, (c) 30 hours, (d) 40 hours, (e)50 hours.

The particles structure after 20 hours of the milling time were irregular and distributed over a wide range particle size. After 40 hours, the particles have become smaller and appear near-spherical shape. The particles appearance were different in size, and the shape became uniform and rounded shape with increasing the milling time.

XRD data of the Fe/Si milled powders are shown in Figure 2. This data was analyzed by qualitative analysis Hanawalt method[19], and it gave information about the possibility of the iron oxide formation (Fe_3O_4/γ-Fe_2O_3) with increasing milling time. This qualitative method analyzed each diffraction data by angle diffraction (2θ) and relative intensity (Ir). These data are registered from the largest to the smallest value for the diffraction line. Diffraction pattern data can be obtained 2θ, d (Å) and Ir as seen in Table. 1.

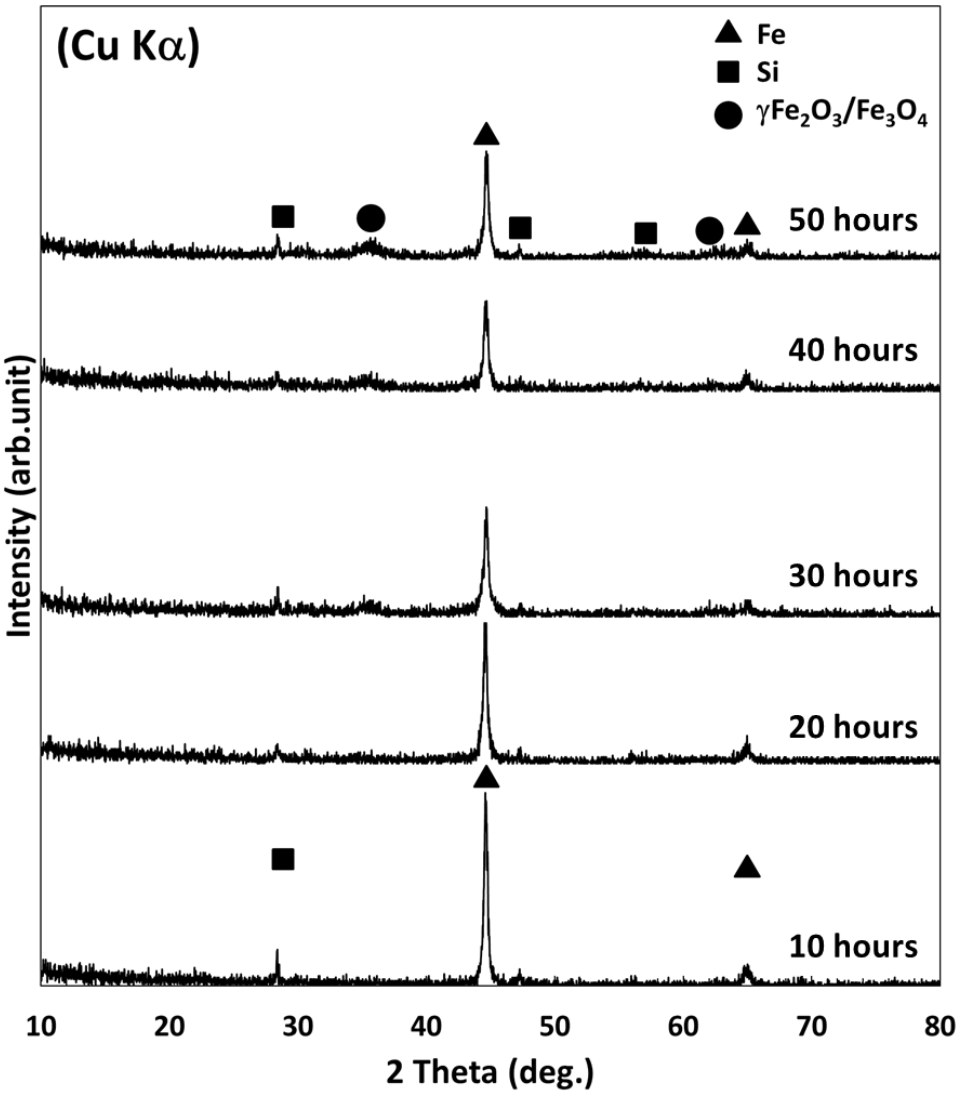

Figure 2. X-ray diffraction pattern of Fe/Si powder after milling 10, 20, 30, 40 and 50 hours

The diffraction intensity of Fe/Si milled powder was diminished on peaks and widened. This appearance means the crystalline size of Fe/Si milled powder becomes smaller than Fe and Si powder. The XRD results were analyzed by Origin software and obtained

diffraction angle (2θ,) and full width at half maximum (FWHM), which is indicated by the β value for each phase Fe, as shown in Table 2. By using the Scherrer equation[19], the average crystalline size can be calculated based on the width of the diffraction peaks:

$$D = (0.9 \cdot \lambda) / (\beta \cdot \cos\theta) \quad (1)$$

D is the crystalline size, Cu-Kα is the wavelength (15.404 nm), β is an FWHM, in radians and θ is diffraction angle. Based on the above equation, the average crystalline size of the milling time can be seen in Table 2. The FWHM of Fe peaks increases with the increase of milling time that indicates refining particles. This result can be seen in the shifts in diffraction angle, which enabled the calculation of crystalline size changes with milling time. Due to the milling process on Fe/Si powders at a different time, the crystalline size decreases up to 40 hours milling time. After 50 hours of milling time, the crystalline size increased, most likely due to the formation of the crystalline growth of Fe powders.

Table 1.The diffraction angle, d-spacing, and relative intensity of Fe/Si milled powder.

Sample	2θ	*d* (Å)	I_r (%)	Remarks
Fe/Si	28.40	3.14	19	Si
(10 hours)	44.58	2.03	100	Fe
	65.08	1.43	2,5	Fe
Fe/Si	28.40	3.14	14	Si
(20 hours)	44.66	2.02	100	Fe
	64.96	1.43	20	Fe
Fe/Si	28.40	3.14	22	Si
(30 hours)	35.54	2.52	12	γFe_2O_3/ Fe_3O_4
	44.66	2.02	100	Fe
	47.22	1.92	14	Si
	62.80	1.47	11	γFe_2O_3/ Fe_3O_4
	65.20	1.42	12	Fe
Fe/Si	28.40	3.14	22	Si
(40 hours)	35.70	2.51	22	γFe_2O_3/ Fe_3O_4
	44.68	2.02	100	Fe
	47.34	1.91	16	Si
	62.28	1.48	13	γFe_2O_3/ Fe_3O_4
	64.88	1.43	24	Fe
Fe/Si	22.04	4.02	14	SiO_2
(50 hours)	28.44	3.13	20	Si
	35.80	2.50	17	γFe_2O_3/ Fe_3O_4
	44.58	2.03	100	Fe
	47.22	1.92	13	Si
	62.90	1.47	11	γFe_2O_3/ Fe_3O_4

Table 2. The diffraction angle. FWHM and crystallite size of Fe/Si milled powders.

Milling time (hours)	2θ	Cos 2θ	FWHM (β)	D
10	44.622	0.92914	0.27195	32.9962
20	44.580	0.92528	0.30147	29.7607
30	44.629	0.92511	0.33049	27.1524
40	44.626	0.92512	0.41426	21.4878
50	44.628	0.92512	0.31575	28.4197

XRD data of the samples for different milling times exhibited a clear indication of the changes in the material. The milled powder showed peaks of the three elements but, after 10 and 20 hours, only the Fe and Si were exhibited. This occurrence means no detectable reactions during the milling to produce any intermetallic compounds and that Si has dissolved in the Fe matrix. XRD data could be attributed to the substitutional dissolution of Si in the α-Fe lattice since the atomic radius of Si (0.118 nm) is smaller than that of Fe (0.123 nm)[20]. The crystalline size of Fe/Si became even more negligible than Fe/Si because the amount of Si dissolved is more significant[18].

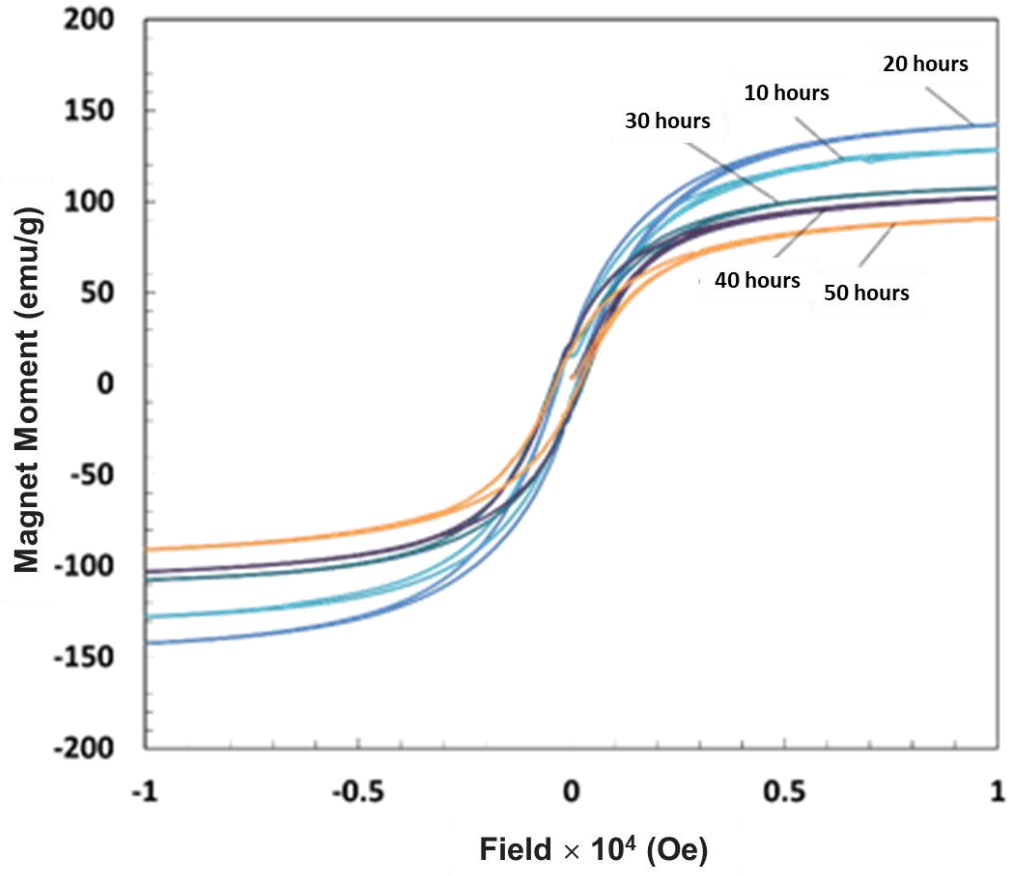

Figure 3. Magnetic hysteresis (M-H) curve measurement results on samples of Fe/Si milled powder.

Table 3. Magnetic parameter of Fe/Si milled powders.

Milling time (hours)	Magnetic parameter		
	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
10	128.9293	17.6145	198
20	142.0172	22.0943	257
30	107.3369	22.8738	354
40	102.0372	22.1424	277
50	90.8423	16.7083	250

Magnetic hysteresis (M-H) curve measurement results on samples of Fe/Si milled powder with different milling time is shown in Figure 3. The curve shows the magnetization value that increases with increasing milling time up to 20 hours and decreases linearly with increasing milling time. It is very closely related to the particle size of the material. The smaller the particle size of the material, has higher the saturated magnetization (*Ms*) value. Referring to the XRD data, the milling time for 10 and 20 hours formed only the primary Fe phase with the lower intensity peak. It suggests that the crystalline size becomes smaller due to the mutual collision between the powders and ball mill. After 30 and 40 hours of milling time, the *Ms* value becomes lower due to the iron oxide formation that influences the magnetic interaction between the iron particles. In comparison, 50 hours milling time showed the smallest *Ms* value due to the formation of iron powder agglomeration.

Results of the M-H hysteresis curve shows several magnetic parameters, such as *Ms*, remanence magnetization (*Mr*) and coercive field (*Hc*). *Ms* value is the maximum value of the magnetic field that can be generated by the material (peak value of hysteresis curve), *Mr* is the value of the magnetic field at the moment when the polarization = 0, and *Hc* is the polarization moment when the magnetic field = 0 divided by 2. The results of the M-H analysis are shown in Table 3. An increase in the *Hc* value materials demonstrated the possibility of a pinning effect on the rotation of the magnetic moment[21]. In addition to the factors mentioned above, the large surface anisotropy and surface roughness of the powders can contribute to their large Hc compared to that of the Fe/Si[22]. Furthermore, the effect of milling on the Fe/Si powders may cause mechanical stress and dislocation, which affected the mechanical properties and is related to the magnetic properties of materials. Hence, the particle size refinement plays a leading role in increasing Hc in that stage, as seen in Figure 1.

CONCLUSION

The effect of milling time on the structure and magnetic properties of Fe-Si was studied in terms of phase transition. The particles appearance were different in size, and the shape became uniform and rounded with increasing milling time. The XRD result showed that the milling time up to 20 hours, which is formed only primary iron phase. In contrast, an increase in milling time up to 50 hours showed an increase in minor phase of iron oxide

(Fe_3O_4/γ-Fe_2O_3) and diminished primary iron phase. The particle size refinement showed a significant role in increasing the coercive field.

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