Annealing Behavior of Ferromagnetic FePt Nanoparticles Prepared in Water in Oil Microemulsions

Koay Mei Hyie[1] and Iskandar Idris Yaacob[2]

Abstract— Monodisperse FePt nanoparticles were prepared by the coreduction of H_2PtCl_6 and $FeCl_2$ precursors in nonionic water/triton X-100/cyclohexane microemulsions. The as-prepared samples with fcc structure were annealed at different temperatures and holding times in forming gas (95% Ar and 5% H_2) atmosphere. X-ray diffraction results showed that a minimum temperature of 650°C was required to initiate the formation of the ordered FePt fct ferromagnetice phase. The coercivity of the sample increased with increasing annealing temperature up to 750°C. Annealing at temperatures above 750°C resulted in grain growth and a drop in coercivity. The lattice parameter of particles decreased when annealing time increased. Annealing at 700°C for longer than 90 minutes caused phase transformation from fct to Pt_3Fe phase. The smallest crystallites size of annealed FePt nanoparticles at 700°C for 90 minutes was 11 nm and they showed the highest coercivity of 3.04 kOe.

***Index Terms*—Annealing, FePt, Microemulsions, Nanoparticles.**

I. Introduction

The application of metallic nanoparticles as a data storage medium is being intensely pursued. Among these, $L1_0$ FePt is the most promising material due to its high value of coercivity and magnetocrystalline anisotropy which makes it possible to overcome superparamagnetism even at a grain size of below 6 nm [1]-[3]. Unfortunately, as-synthesized monodispere FePt nanoparticles are usually face-centered cubic (fcc) and must be annealed to high temperatures to transform them to face-centered tetragonal (fct) phase [4]. High temperatures are required for the transformation, but they also cause sintering and formation of agglomerates [1]. Therefore, annealing temperature should be carefully selected to minimize these unwanted effects.

This work was supported in part by UPDit, University of Malaya under Grant FR076/2007A and FP036/2007C.

Koay Mei Hyie and Iskandar Idris Yaacob are with Center for Nanotechnology, Precision and Advanced Materials, University of Malaya, 50603 Kuala Lumpur, Malaysia. (email: hyie1105@yahoo.com, iskandar@um.edu.my)

In this study, we synthesize monodisperse FePt nanoparticles using water in oil microemulsions. This technique is unique because of the presence of surfactant that can effectively prevent excess aggregation of particles [5]. We also investigate the annealing behavior of FePt nanoparticles in forming gas (95% argon gas and 5% hydrogen gas) atmosphere.

II. Experiment Methods

FePt nanoparticles at molar ratio of 1:1 were prepared using $FeCl_2$, H_2PtCl_6, and N_2H_5OH (hydrazine hydrate) as precursors. Two quaternary microemulsion solutions (Triton X-100/water/cyclohexane/pentanol) were formed. The first one contained an aqueous solution mixture of Fe^{2+} and Pt^{4+} and the second one contained an aqueous solution of hydrazine. The coreduction process was initiated when the microemulsion solution containing hydrazine was poured into the microemulsion solution containing Fe^{2+} and Pt^{4+} under gentle stirring. Black precipitates were formed within a few seconds indicating the coreduction process. The precipitates were recovered and then washed with acetone to remove excess surfactant followed by rinsing with deionized water for several times. The as-synthesized nanoparticles were finally dried at room temperature. The as-synthesized FePt nanoparticles were annealed at different temperatures: 600°C, 650°C, 700°C, 750°C, and 800°C for 30 minutes under forming gas (95% argon + 5% hydrogen) atmosphere. The optimum temperature was selected from this investigation and the effect of annealing times on phase transformation of FePt nanoparticles was then studied from 30 minutes to 120 minutes.

The phase transformation of the FePt nanoparticles were investigated by a Philips X-Pert MPD X-ray diffractometer (XRD) using a standard θ -2θ configuration with Cu-Kα radiation (λ = 0.1542 nm). Transmission electron microscopy studies were carried out using a Leo Libra 120 Transmission Electron Microscope (TEM) operated at 80 kV. The coercivity of the FePt nanoparticles was obtained using an Alternating Gradient Magnetometer (AGM) with maximum applied fields of ±10 kOe at room temperature.

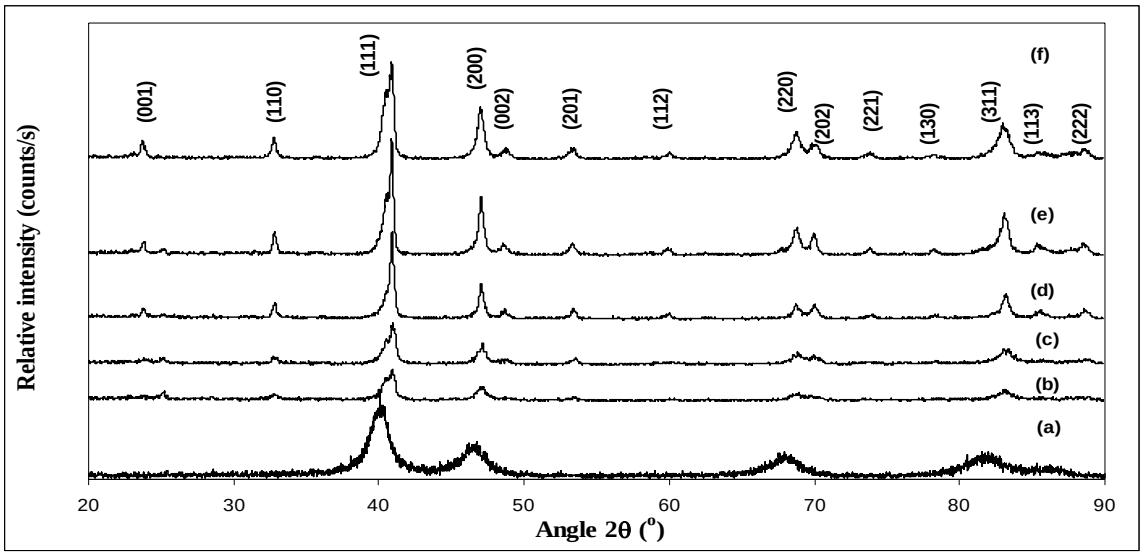

Fig.1. XRD patterns of FePt nanoparticles at different annealing temperatures for 30 minutes. (a) as-synthesized (b) annealed at 600°C (c) annealed at 650°C (d) annealed at 700°C (e) annealed at 750°C (f) annealed at 800°C

I. RESULTS AND DISCUSSION

A. *Effect of Annealing Temperature*

Fig. 1 shows XRD patterns for as synthesized and annealed FePt nanoparticles at different temperatures for the same holding time (30 minutes). The XRD pattern of the as-synthesized FePt nanoparticles reveals a typical disorderd fcc structure, which is indicated by the appearance of (111) and (200) at 2θ angles of about 40º and 47º. After annealing at 600°C, FePt nanoparticles are still having fcc structure. The phase transformation from disordered fcc to long range ordered fct phase only occurs when annealing temperature is above 650°C. This is evident in the XRD patterns with the appearance of the superlattice reflections (001) and (002) at 2θ angles of about 24º and 49º, respectively. Further confirmation of long range chemical ordering can be seen as a result of splitting of the (200) and (220) peaks to give the (002) and (202) peaks, respectively. The splitting is due to the tetragonal symmetry of fct FePt ($a \neq c$) [6]. The intensities of peaks that reflect chemically ordered phase increase with increasing annealing temperature, suggesting an improvement in an atomic ordering of Fe and Pt in fct structure.

The crystallite sizes calculated from XRD peak broadening using Scherrer's formula and coercivities (*Hc*) of annealed FePt nanoparticles are presented in Fig. 2. The crystallite size increases as the annealing temperature is increased. This may be due to coalescence of the particles at higher temperature [7]. The largest crystallite size is obtained for FePt nanoparticles annealed at 700°C. The sudden increase in crystallite size may due to the volume expansion in fct FePt. The *Hc* also increases with increasing annealing temperature due to better chemical ordering of Fe and Pt in fct structure. However, sintering process at above 800°C cause *Hc* to decrease due to grain growth.

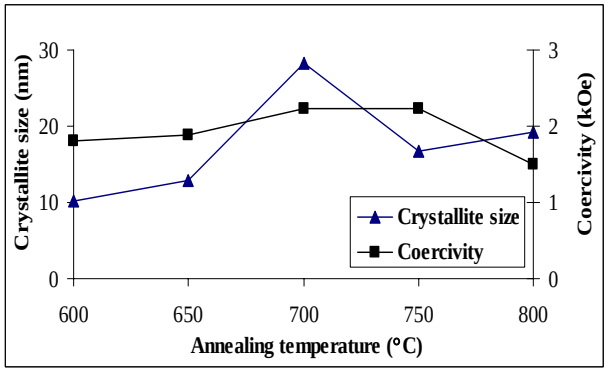

Fig. 2. Crystallite size and coercivity of annealed FePt nanoparticles at different annealing temperatures.

B. *Effect of Annealing Times*

Fig. 3 shows XRD patterns of FePt nanopartilces annealed at 700°C for different annealing times. Phase transformations from fcc to fct begins after 30 mins. This is indicated by appearance of superlattice reflections of (001) and (002) at 2θ angles of about 24º and 49º, respectively in the XRD pattern. The crystallite size decreases with increasing annealing time as indicated by decrease in width of the XRD peak. Annealing time longer than 90 minutes causes phase transformation from fct to Pt_3Fe phase. This is indicated by XRD pattern of sample annealed for 120 mins (Fig. 3e) where the (002) and (202) peaks of fct are absent.

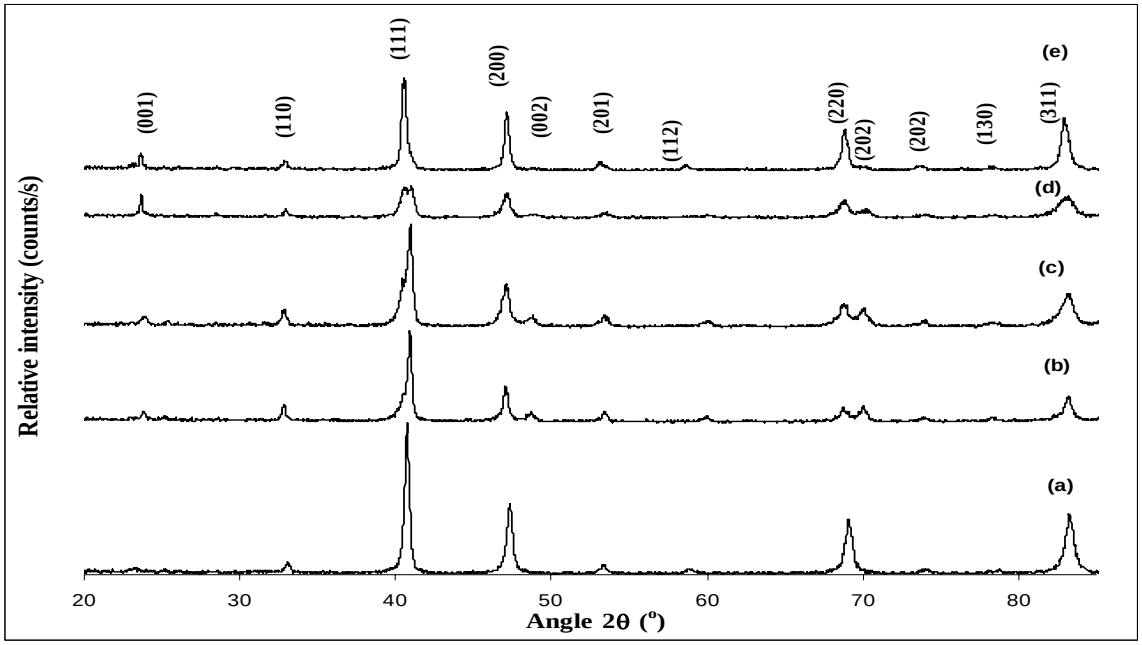

Fig. 3. XRD patterns of FePt nanoparticles annealed at 700°C for different annealing times. (a) 10mins (b) 30 mins (c) 60 mins (d) 90 mins (e) 120 mins

The effect of annealing time on the physical and magnetic properties of FePt nanoparticles is summarized in Table I. The crystallite size of as synthesized FePt nanoparticles is 5.8 nm. After annealing, the crystallite size increases.

The ordering parameter (*S*) of fct FePt nanoparticles is calculated using (1):

$$S \cong 0.85\left[\frac{I_{001}}{I_{002}}\right]^{1/2} \quad (1)$$

Where I_{001} and I_{002} are the integrated intensities of the (001) and (002) diffraction peaks from the XRD patterns [8].

Table I. The physical and magnetic properties of as-synthesized and annealed FePt nanoparticles at 700°C for different annealing times.

Annealing Time (mins)	Crystallite Size (nm)	Degree of Ordering *S*	Lattice Parameter *a* (nm)	Coercivity *Hc* (kOe)
As-synthesize	5.8	-	-	0.048
10	39.9	-	-	0.594
30	28.3	0.79	0.3865	2.233
60	16.8	0.82	0.3851	2.704
90	11.0	0.90	0.3832	3.044
120	35.7	-	-	2.641

When FePt nanoparticles are annealed at 700°C from 30 mins to 90 mins, the crystallite size decreases. The degree of ordering is however increases. This may be due to a change of volume during the phase transformation. The lattice constant for fcc FePt phase reported [9] is 0.387 nm whereas the lattice constant for fct FePt phase is 0.385 nm [10]. From our experimental results, shrinkage occurs when the FePt nanoparticles is annealed. The decrease of lattice parameter is possibly due to rearrangement of Fe and Pt atoms in the structure during the transformation from fcc to fct phase.

When fcc FePt transforms to fct, its *Hc* becomes very high because the annealed sample is a strong ferromagnet. When annealing time is longer, the coercivity increases due to better chemical ordering. The FePt nanoparticles annealed at 700°C for 90 mins show the highest coercivity which is 3.044 kOe. However, increasing annealing time beyond 90 mins cause reduction of coercivity because of the existence of Pt_3Fe phase.

C. TEM Micrograph

TEM micrograph of FePt nanoparticles annealed at 700°C for 90 mins is shown in Fig. 4. The particles are almost spherical and quite monodispersed. The mean physical diameters of the samples obtained by measuring the diameters of more than 100 particles is about 15.7 nm. The physical diameter agrees well with the XRD crystallite sizes indicating that the particles are mostly monocrystals.

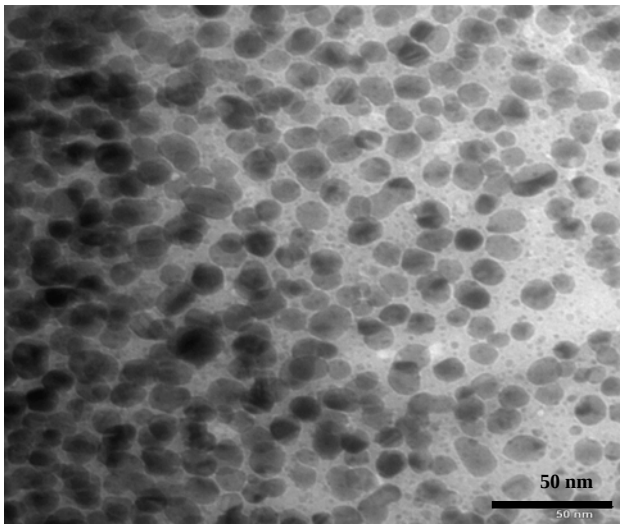

Fig. 4. TEM micrograph of FePt nanoparticles annealed at 700°C for 90 mins.

REFERENCES

[1] M. Tanase, N. T. Nuhfer, D. E. Laughlin, T. J. Klemmer, C. Liu, N. Shukla, X. Wu and D. Weller, "Crystallographic ordering studies of FePt nanoparticles by HREM", *J. Magn. Magn. Mater.*, vol. 266, Mar. 2003, pp. 215-226.

[2] T. Iwaki, Y. Kakihara, T. Toda, M. Abdullah and K. Okuyama, "Preparation of high coercivity magnetic FePt nanoparticles by liquid process", *J. Appl. Phys.*, vol. 94, no. 10, Nov. 2003, pp. 6807-6811.

[3] S. Anders, M. F. Toney, T. Thomson, J. U Thiele, B D. terries, S. Sun, and C. B. Murray, " X-ray studies of magnetic nanoparticles assemblies", *J. Appl. Phys.*, vol. 93, no. 10, May 2003, pp. 7343-7345.

[4] Y. Ding, S. A. Majetich, J. Kim, K. Barmak, H. Rollins and P. Sides, "Sintering prevention and phase transformation of FePt nanoparticles", *J. Magn. Magn. Mater.*, vol. 284, Aug. 2004, pp. 336-341.

[5] M. L. Wu, D. H. Chen and T. C. Huang, "Preparation of Pd/Pt bimetallic nanoparticles in water/AOT/isooctane microemulsions", *Journal of Colloid and Interface Science*, vol. 243, Sep. 2001, pp. 102-108.

[6] O. Robach, C. Quiros, S. M. Valvidares, C. J. Walker and S. Ferrer, "Structure and Pt magnetism of FePt nanoparticles investigated with X-ray diffraction", *J. Magn. Magn. Mater.*, vol. 264, Jan 2003, pp. 202-208.

[7] W. H. Tzu, H. H. Yen, T. H. Tu and C. H. Lee, "X-ray diffraction and absorption spectroscopy studies of the structure of self-assemble FePt nanoparticles during annealing", *J. Magn. Magn. Mater.*, vol. 282, May 2004, pp. 127-130.

[8] C. B. Rong, D. Li, V. Nandwana, N. Poudyal, Y. Ding, Z. L. Wang, H. Zeng and J. P. Liu, "Size-dependent chemical and magnetic ordering in $L1_0$- FePt nanoparticles", *Adv. Mater.*, vol. 18, Sep. 2006, pp. 2984-2988.

[9] JCPDS-International Centre for Diffraction Data 1975 Card no. 29-0717.

[10] JCPDS-International Centre for Diffraction Data 1992 Card no. 43-1359.