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Research Article

Magnetic Properties of FePt Nanoparticles Prepared by Sonoelectrodeposition

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Sonoelectrodeposition is a useful technique to make metallic nanoparticles, using ultrasound during electrodeposition to remove nanoparticles as they grow on the cathode surface. This paper reports some structural and magnetic properties of FePt nanoparticles prepared by this method. The as-prepared $Fe_{45}Pt_{55}$ nanoparticles were ferromagnetic at room temperature. Upon annealing at 700°C for 1 h under H_2 atmosphere, the saturation magnetization and the coercivity of the nanoparticles were improved significantly. The annealed nanoparticles showed a high coercivity of 13.5 kOe at 2 K and of 9 kOe at room temperature. Sonoelectrodeposition is a promising technique to make large quantity of FePt nanoparticles.

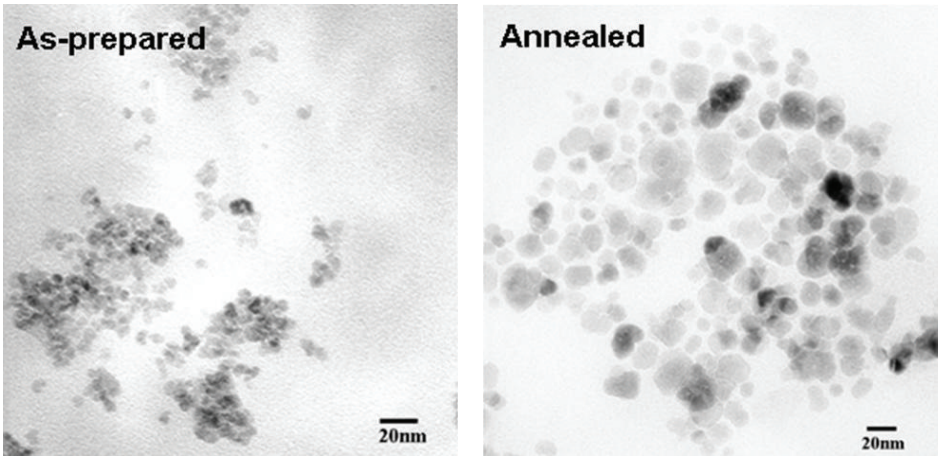
1. Introduction

The ordered face-centered tetragonal (fct) $L1_0$ FePt materials are normally obtained from the disordered face-centered cubic (fcc) materials via the order-disorder transition. The ordered FePt alloys possess excellent hard magnetic properties with the saturation magnetization, $\mu_0 M_s$, of 1.4 T, the Currie temperature, T_c, of 750 K, and the crystalline anisotropy K_1, of 7 MJ/m^3 [1]. Despite the high cost of Pt, FePt thin films or particles have been paid much attention to their use as ultrahigh density magnetic storage media and microelectronic mechanical system (MEMS) due to the mechanical and chemical stability of the ordered fct $L1_0$ structure.

There are several ways to make FePt-nanostructured materials including physical techniques such as mechanical deformation [2], arcmelting [3], vacuum evaporation (sputtering and thermal evaporation) [4, 5], laser ablation pulse [6], chemical methods [7–9], and physicochemical method such as electrodeposition [10, 11]. Up to now, the vacuum evaporation is the most used method. Electrodeposition is a promising way to obtain FePt thin films because it is less expensive than physical methods, less complicated than chemical methods. But by this technique, it is difficult to get nanoparticles with large quantity. Sonoelectrochemistry was developed to make nanoparticles [12]. It combined the advantages of sonochemistry and electrodeposition. Sonochemistry is a very useful synthetic method which was discovered as early as 1934 that the application of ultrasonic energy could increase the rate of electrolytic water cleavage. The effects of ultrasonic radiation on chemical reactions are due to the very high temperatures and pressures, which develop in and around the collapsing bubble [13]. Sonoelectrochemistry has the potential benefit of combining sonochemistry with electrochemistry. Some of these beneficial effects include acceleration of mass transport, cleaning and degassing of the electrode surface, and an increased reaction rate [14]. In this paper, we report the use of the sonoelectrochemical method for the preparation of FePt nanoparticles. Recently, CoPt nanoparticles encapsulated in carbon cages prepared by sonoelectrodeposition have been reported by Luong et al. [15].

2. Experimental

The sonoelectrochemical device employed is similar to that described in [16]. A titanium horn with diameter of 1.3 cm acted as both the cathode and ultrasound emitter (Sonics



(a) (b)

Figure 1: TEM images of the as-prepared (a) and annealed (b) $Fe_{45}Pt_{55}$ nanoparticles (700°C/1 h).

VCX 750). The electroactive part of the sonoelectrode was the planar circular surface at the bottom of the Ti horn. An isolating plastic jacket covered the immersed cylindrical part. This sonoelectrode produced a sonic pulse that immediately followed a current pulse. One pulse driver was used to control a galvanostat and the ultrasonic processor, which was adapted to work in the pulse mode. A home-made galvanostat (without using a reference electrode) was used to control the constant current regime. A platinum plate with a square of 1 cm^2 was used as a counter electrode. The current pulse was 15 mA/cm^2. The ultrasound power density was 100 W/cm^2. The duration t_{on} of the current pulse was 0.5–0.8 s, then the current was turned off for a fixed duration t_{off} of 0.5 s. During t_{on}, FePt nanoparticles were deposited on the surface of the electrode. When the current was switched off, an ultrasound was activated to remove the nanoparticles from the electrode. The time of ultrasound was 0.3 s. The temperature during the reaction was room temperature. The volume of the electrolysis cell was 80 mL containing 1 mM H_2PtCl_6, 0.1 M $FeSO_4$, and 0.525 M Na_2SO_4. The chemicals were mixed under N_2 atmosphere. The pH = 3 of the solution was controlled by H_2SO_4. After deposition, FePt nanoparticles were collected by using a centrifuge (Hettich Universal 320, 9000 rpm, 20 min). Nanoparticles were dried in air at 80°C for 20 min. All samples were annealed at 700°C for 1 h under H_2 atmosphere. The structure of the nanoparticles was analyzed by using a Bruker D5005 X-ray diffractometer (XRD). The particle morphology was obtained from a transmission electron microscope (TEM JEM1010-JEOL). The chemical composition of the FePt nanoparticles was studied by using an energy dispersion spectroscopy (EDS OXFORD-ISIS 300) and revealed that the chemical composition of our sample is $Fe_{45}Pt_{55}$. Magnetic measurements were conducted by using Quantum Design's superconducting quantum interference device (SQUID) with a magnetic field up to 50 kOe at temperature range from 2 K to 300 K.

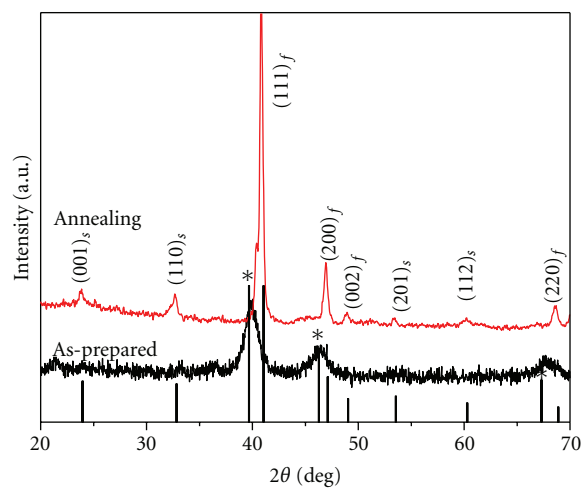


Figure 2: XRD patterns (Cu Kα radiation) of the as-prepared (bottom) and annealed (top) $Fe_{45}Pt_{55}$ nanoparticles compared to those of the intensities for $L1_0$ FePt (PDF file 431359) and for Pt (marked by the asterisks, PDF file 04–0802). The fundamental peaks of FePt structure were denoted by "f," and the superlattice peaks were denoted by "s."

3. Results and Discussion

Figure 1 is the TEM images of typical as-prepared and annealed samples. Particle size of the as-prepared $Fe_{45}Pt_{55}$ sample was 5–10 nm. After annealing the particle size increased to 10–25 nm due to the aggregation and particle growth. In addition, the size distribution of the annealed particles was larger than that of the as-prepared samples.

Figure 2 shows the XRD patterns of the as-prepared and the annealed $Fe_{45}Pt_{55}$ nanoparticles (700°C for 1 h). Before annealing, the XRD results showed the reflections of pure Pt structure, which is similar to other FePt thin films produced by electrodeposition [17]. However, authors in

[17] thought that the reflections were from the disordered fcc phase. For the fcc phase, XRD results present only the fundamental reflections which are (111), (200), and (220). The fundamental reflections of the fcc FePt are close to the (111), (200), and (220) reflections of the Pt that make some scientists thought that they are of the fcc structure. We propose that XRD results from our as-prepared nanoparticles and from [17] are the peaks of only Pt. The reflections from Fe are very weak due to the fact that their atomic weight is much less than that of Pt which is similar to the XRD result of FePt foils prepared by cold deformation [18]. The Pt peaks in the as-prepared samples are broad due to the small size of the particles. Using the Scherrer formula with the full width at half maximum of the strongest peak (111), the mean particle size of Pt particles was deduced to be 5.2 nm, which is much smaller than the particle size obtained from the TEM image. The particles were not disordered FePt, but they can be formed by many small domains of pure Fe and Pt. The formation of FePt by electrodeposition did not occurr and may be ascribed to the large difference in the standard electrode potential of the Fe^{2+}/Fe (−0.44 V [19]) and Pt^{4+}/Pt (0.742 V [20]). Upon annealing, the formation of the ordered $L1_0$ fct phase happened by the diffusion process between Fe and Pt domains.

Magnetic measurements revealed low-saturation magnetization (M_s) and coercivity (H_c) in all as-prepared samples (data not shown). The saturation magnetization of the unannealed particles was about few emu/g and the coercivity was 20–80 kOe. The low value of M_s of the as-prepared nanoparticles may be explained by the oxidation or hydroxidation of Fe atoms in nanoparticles, which can result in the weak magnetic iron oxides and iron hydroxides. This is in agreement with the suggestion of separated Fe and Pt domains in as-prepared nanoparticles. It is known that FePt with high-saturation magnetization is a chemically stable material. Therefore, it is difficult to be oxidized to form weak ferromagnetic materials. After annealing, the hard magnetic FePt phase was formed. Figure 3 presents the magnetic curves of the annealed $Fe_{45}Pt_{55}$ at different temperatures. The curves show a typical hard magnetic hysteresis loops with high H_c. Beside, form of the magnetic curves shows that a small soft magnetic phase, probably $FePt_3$, exists in the sample. The as-prepared $Fe_{45}Pt_{55}$ nanoparticles were ferromagnetic at room temperature. Upon annealing at 700°C for 1 h, the saturation magnetization and the coercivity of the nanoparticles were improved significantly. Coercivity of annealed $Fe_{45}Pt_{55}$ nanoparticles as a function of temperature is shown in Figure 4. At 2 K, the coercivity is 13.5 kOe and slightly decreases with increasing temperature to the value of 9 kOe at 300 K.

Magnetic squareness $S = M_r/M_s$ of annealed $Fe_{45}Pt_{55}$ nanoparticles as a function of temperature is shown in Figure 5. The temperature dependence of S is similar to that of H_c. At 2 K, the magnetic squareness is 0.78, slightly decreases with increasing temperature, and has a value of 0.745 at 300 K. This value of S is very close to that obtained for $L1_0$CoPt nanoparticles at room temperature [15].

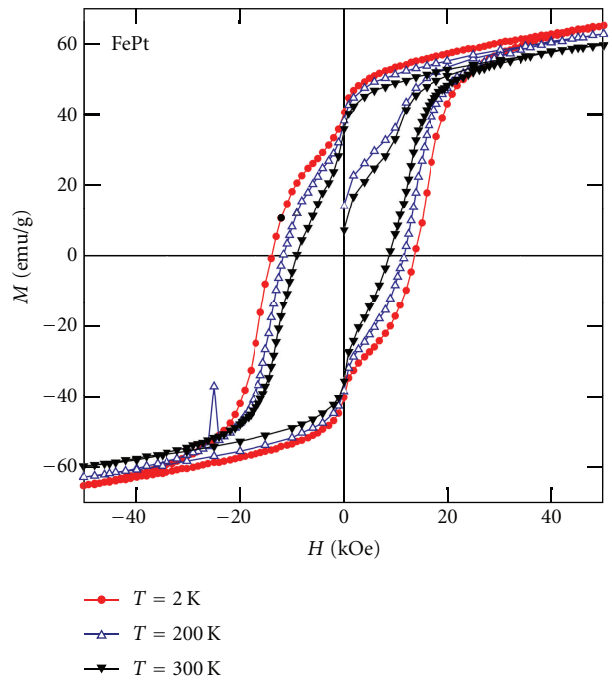


Figure 3: Magnetic curves of annealed $Fe_{45}Pt_{55}$ nanoparticles at different temperatures.

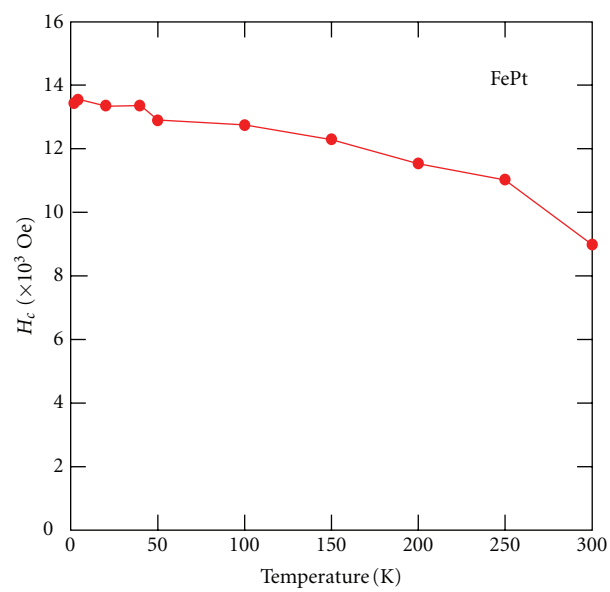


Figure 4: Coercivity of annealed $Fe_{45}Pt_{55}$ nanoparticles as a function of temperature.

4. Conclusion

Sonoelectrochemistry is a promising method to make FePt magnetic nanoparticles. The annealed FePt nanoparticles made by this technique had the size of 10–25 nm. After annealing, the nanoparticles showed a high coercivity of 13.5 kOe at 2 K and 9 kOe at room temperature. This method possesses some advantages compared to common methods

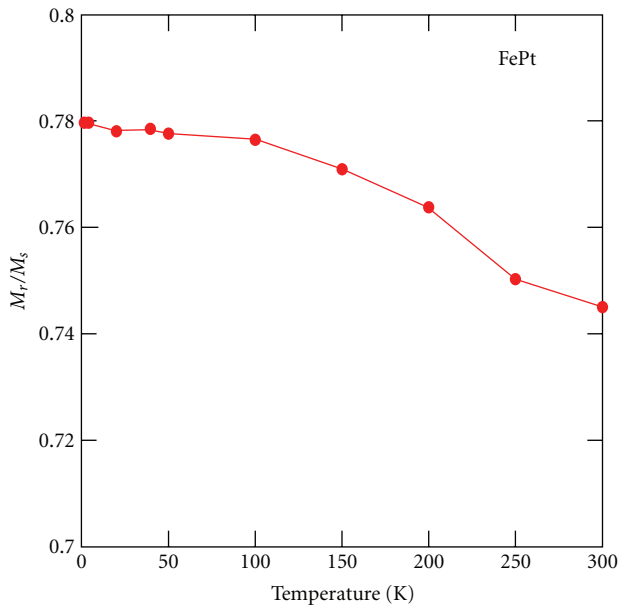


Figure 5: Magnetic squareness $S = M_r/M_s$ of annealed $Fe_{45}Pt_{55}$ nanoparticles as a function of temperature.

such as simple preparation, low-cost equipment, and easy scaleup.

Acknowledgments

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