The Effect of NaCl prepared by ultra-sonic vibration on Sintering of annealed FePt nanoparticles

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Abstract. FePt nanoparticles were synthesis via high-temperature solution phase. Monodispersed 3.5 nm FePt nanoparticles were first obtained by reduction of FeCl₂.4H₂O and Pt(acac)₂. These preformed FePt nanoparticles were then combined with NaCl to prevent from sintering after annealing. The 1 micron salt particles were fabricated by ultra-sonic vibration method and used as the separating media. Annealing studies show that these salt-matrix FePt nanoparticles are stable after annealing at 700 °C for 4 h. The annealed FePt particles diameter increases from 4 to 25 nm as observed by TEM. The magnetic properties are largely affected by annealing temperature. The role of these salt particles on sintering of annealed FePt nanoparticles has been investigated.

1. Introduction

L₁₀ FePt nanoparticles have a large magnetocrystalline anisotropy and, thus, exhibit large coercivity at room temperature, even when their size is as small as several nanometers. FePt nanoparticles have been intensively studied for many applications such as high-density recording media [1-3] and ferromagnetic nanocomposites [4]. Undesirable sintering between nanoparticles, which takes place when nanoparticles are annealed to transform the crystalline structure from the chemically disordered face-centered cubic (fcc) to the chemically ordered L₁₀ phase (face-centered tetragonal), should be avoided [5]. Among currently available techniques for preparing FePt nanoparticles, wet chemical methods produce the nanoparticles with well controlled particle size and size distribution. Unfortunately, as-synthesized FePt nanoparticles always have fcc structure and have no magnetic ordering at room temperature. Heat treatments to convert the fcc structure to the face-centered tetragonal (fct) structure with high magnetic anisotropy must be performed at elevated temperatures (>600 °C) which undesirably lead to the particle agglomeration and sintering.
To solve this dilemma, extensive efforts have been made since 2000 to obtain monodisperse fct FePt nanoparticles. One of the approaches in such efforts is to lower the onset temperature for the fcc to fct phase transformation. Doping by elements such as Ag, Au, and Cu in the FePt phase was tested resulting in the onset of the fct phase at 400 °C [6, 7]. Direct synthesis of the fct structured particles by the polyol process using high boiling point solvents is another major approach [8–11]. In this approach, higher synthesis temperatures can be applied which allows partial formation of the fct phase. Recently, methods have been tested to coat the fcc FePt nanoparticles with high-melting-point materials and then to anneal the mixture to obtain the fct nanoparticles without sintering. Immiscible silica matrix [5], polyethyleneimine linker molecules [12], SiO shells [13,14] and TiO matrix [15] were used as the high-melt-point materials. The advantage of this coating approach is that high temperature annealing can be performed without causing particle sintering. The coating materials cannot be easily removed after the annealing so that these methods are not suitable in large quantity monodisperse magnetic nanoparticles free of nonmagnetic impurities. Other approaches to obtaining monodisperse fct nanoparticles include rapid thermal annealing [16] and pulse laser annealing [17]. To date, however, it is still a very challenging task to obtain both high coercivity and monodisperse morphology simultaneously of fct FePt nanoparticles. Most reported results show a trade-off between the two properties. It is, therefore, highly desirable to find processing techniques to produce completely transformed fct FePt monodisperse nanoparticles. A new technique has been adopted, based on salt-matrix annealing at temperatures up to 700 °C, with which monodisperse fct FePt nanoparticles have been successfully produced [18].

In this invited paper we present our recent research results in producing ferromagnetic FePt nanoparticles by salt-matrix method. We will demonstrate that the size of NaCl prepared by ultra-sonic vibration affects on diameter of FePt nanoparticles during the salt-matrix annealing.

2. Experimental details

The fcc FePt nanoparticles with size of 3.5 nm were prepared using the synthesis described by sun et al. [1]. Synthesis of the nanoparticles, involves the reduction of Pt(acac)2 and FeCl2·4H2O, in phenyl ether solvent in presence of 1,2-hexadecanediol. The oleic acid and oleylamin surfactants were added to solvent, at 100 °C, as a protective agent in order to prevent agglomeration and oxidation. By adding superhydride (LiBEt3H) under a blanket of N2 at 200 °C, followed by refluxing, the FePt nanoparticles were formed. The refluxing temperature was fixed at 245 °C for 30 min. The black reaction mixture was cooled to room temperature and then combined with ethanol to remove the impurity. The product was precipitated and separated by centrifugation (8000 rpm, 10min). Any undissolved material was removed by centrifugation. Then nanoparticles were dispersed in hexane in presence of surfactants.

Sodium chloride (NaCl) was selected as a separating media in this investigation due to its chemical stability and high solubility in water. The salt particles were produced by two different methods: (i) The salt powder was crumbled by mechanical ball-milled for more than 24 h to reach particle size smaller than 20 microns. The ball-milled NaCl powder was then dispersed in hexane. (ii) Pure NaCl powder was solved in de-ionized water to reach saturation and then hexane solution was added to the saturated solution of salt water and ultra-sonic vibration was applied simultaneously. Ultra-sonic vibration led to formation and dispersion of the 1 micron salt crystallized particles in hexane phase.

The salt particles were mixed with hexane dispersion of 3.5 nm as-synthesized fcc FePt nanoparticles. The mixture was stirred until all the solvent evaporates at room temperature and then annealed in forming gas (93%Ar +7%H2) to complete the fcc to fct transition. The NaCl-to-FePt weight ratio 100:1 was chosen and annealing temperature fixed at 700 °C for 4 h. The annealed mixture which salts prepared using method (i) washed in de-ionized water and centrifuged for several times to remove all the NaCl particles and for nanoparticles which salts prepared by method (ii) washing process did not necessary because the fine salt particles removed from nanoparticles and dispersed in hexane [18]. The effect of NaCl on FePt particle size was investigated by each of the two salt preparation methods. Morphology of FePt nanoparticles before and after annealing was observed.
by a transmission electron microscope (TEM) analysis using a Philips EM 208 TEM (100KV) with resolution 200KX. To determine the nanoparticles structure, the X-ray diffraction (XRD) measurement was prepared after evaporation of hexane on a Silicon wafer using a Seifert with Cu-Kα (wavelength = 1.54 Å) radiation. The magnetization of the FePt samples in a variable magnetic field was measured using a vibrating sample magnetometer (VSM) model PAR-155.

3. Results and discussion

Figure 1 shows XRD patterns of the as-synthesized and annealed FePt nanoparticles; the annealing was done in forming gas at 700 °C for 4 h. The as-synthesized 3.5 nm particles exhibit a disordered fcc structure with lattice constant 3.871 Å which comply with the report made on FePt structures analysis [18]. The X-ray patterns confirm that the annealing in the salt-matrix transforms the disordered fcc structure into the tetragonal L1₀ structure. Because of the small particle size, the peaks are very broad and hence overlap each other. The average particle diameter estimated from scherrer’s formula is consistent with that determined by statistical analysis of the TEM images (figure 3), indicating that each individual particle is a single crystal.

![XRD Patterns](image)

**Figure 1.** XRD patterns of the (a) as-synthesized and (b) annealed FePt nanoparticles at 700 °C for 4 h with NaCl : FePt ratio 100:1.

![TEM Image](image)

**Figure 2.** The image of 1 micron salt particles prepared by ultra-sonic vibration method.

![TEM Image](image)

**Figure 3.** TEM image of the 3.5 nm as-synthesis FePt nanoparticles.
Figure 2 show the image of the salt particles fabricated by ultra-sonic vibration method with salt water concentration of 190 mg/mL and an average salt particle size about 1 micron and ultrasonic duration of 45 min. Figure 3 indicates TEM image of the as-synthesized fcc FePt nanoparticles. The particles prepared at 245 °C, have an average diameter of about 3.5 nm and narrow size distribution with standard deviation of about 8%.

![Figure 2](image1.png)

**Figure 2.** TEM images of the salt particles fabricated by ultra-sonic vibration method with salt water concentration of 190 mg/mL and an average salt particle size about 1 micron and ultrasonic duration of 45 min.

Figure 4 shows the TEM images of annealed FePt nanoparticles at 700 °C for 4 h. The annealed (a) 15 and (b) 4.5 nm fct FePt particles before and after ultra-sonic vibration without NaCl; (c) 10 and (d) 4.5 nm with ultra-sonic duration of 15 and 30 min with NaCl; (e) 25 and (f) 4.5 nm with and without NaCl after ultra-sonic vibration. The TEM images of (g) and (h) show the effect of stabilizers on L1₀ FePt particles with and without surfactants respectively.

![Figure 4](image2.png)

**Figure 4.** TEM images of fct FePt nanoparticles annealed at 700 °C for 4 h. The annealed (a) 15 and (b) 4.5 nm fct FePt particles before and after ultra-sonic vibration without NaCl; (c) 10 and (d) 4.5 nm with ultra-sonic duration of 15 and 30 min with NaCl; (e) 25 and (f) 4.5 nm with and without NaCl after ultra-sonic vibration. The TEM images of (g) and (h) show the effect of stabilizers on L1₀ FePt particles with and without surfactants respectively.
surfactants with 2:1 ratio. It can be seen that the stabilizers control the spaces between nanoparticles and the dispersity and stability of fct FePt particles increases.

Figure 5 shows the results of magnetic measurements before and after heat treatments. It indicates that as-synthesized FePt nanoparticles was first superparamagnetism at room temperature and after annealing under forming gas at 700 °C for 4 h, the saturation magnetization increases to 45 emu/g and coercivity raises to 7.5 kOe. These results confirm the suitable magnetic property of nanoparticles.

4. Conclusions

Salt (NaCl)-matrix annealing, an easy-handling method, has been developed to produce fct FePt nanoparticles. It has been realized that the salt particles prepared by ultra-sonic vibration method make well-separated annealed FePt nanoparticles related to NaCl fabricated by ball milled method. The effects of ultra-sonic vibration, ultra-sonic duration, salt removing and surfactant stabilizers on fct FePt nanoparticles were investigated and realized that each of parameters can be important in size decreasing and stabilizing of the FePt nanoparticles. We found the following: (i) The size of L1₀-FePt particles was decreased from 25 nm to 5 nm by ultra-sonic vibration action. (ii) The diameter of annealed nanoparticles was decreased from 10 to 4.5 nm as a result of increasing the ultra-sonic duration from 15 to 30 min. (iii) Due to salt removing from fct FePt particles by de-ionized water the diameter of nanoparticles was decreased from 25 nm to 4.5 nm. (iv) The average distance between 4 nm FePt nanoparticles was controlled by using surfactant stabilizers. Finally (v) in purification stage the NaCl prepared by ultra-sonic vibration method was removed from fct FePt particles without washing. In conclusion, the NaCl fabricated by ultra-sonic vibration method make more advantageous annealed FePt nanoparticles in size and particles dispersion as compared to the ball milled method.

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