Monodisperse face-centred tetragonal FePt nanoparticles with giant coercivity

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Abstract
Monodisperse face-centred tetragonal (fct) FePt nanoparticles with high magnetic anisotropy and, therefore, high coercivity have been prepared via a new heat treatment route. The as-synthesized face-centred cubic FePt nanoparticles were mixed with salt powders and annealed at 700°C. The salts were then removed from the particles by washing the samples in water. Monodisperse fct FePt particles were recovered with the particle size and shape being retained. Coercivity of the isolated particles up to 30 kOe at room temperature has been obtained.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetic nanoparticles with high anisotropy are essential for advanced applications such as high density magnetic recording media [1], high performance permanent magnets [2] and sensors and drug carriers in biomedical technology [3]. It was not till several years ago when Sun *et al* [1] reported their breakthrough in the chemical synthesis of FePt nanoparticles that people could prepare monodisperse nanoparticles of a hard magnetic composition with uniform particle size and chemical stability. The as-synthesized FePt nanoparticles, unfortunately, are face-centred cubic (fcc) structure which does not provide the magnetocrystalline anisotropy required for the applications mentioned above. The face-centred tetragonal (fct) FePt composition has very high magnetocrystalline anisotropy. However, to transform the fcc structured nanoparticles to the fct structure, heat treatment at temperatures above 500°C is necessary. Undesirable coalescing and sintering of the nanoparticles also take place at these temperatures, which keeps the dream of direct application of monodisperse hard magnetic nanoparticles unrealized.

Extensive efforts have been made since the year 2000 to obtain monodisperse fct FePt particles. One of the approaches, in such efforts, is to lower the onset temperature for the fcc to the 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 [4–9]. The direct synthesis of the fct

structured particles by the polyol process using high boiling point solvents is another major approach [10–13]. In this approach, higher synthesis temperatures can be applied which allow partial formation of the fct phase. Recently, fcc FePt nanoparticle arrays with coating were annealed at temperatures higher than 700°C without sintering. Immiscible silica matrix [14] or polyethyleneimine linker molecules [15] was used as the coating material. The coating approach, however, was suitable only for monolayers of the separated nanoparticles on substrates. Other approaches for obtaining monodisperse fct nanoparticles include rapid thermal annealing [16] and pulse laser annealing [17]. To date, all the reported approaches have been successful only in obtaining partially transformed fct nanoparticles while high coercivity has not been developed from the partially transformed particles. It is, therefore, highly desirable to find processing techniques for producing completely transformed fct FePt nanoparticles.

2. Experimental procedure

Our experimental concept is based on the separation between the FePt nanoparticles during annealing. After testing different organic and inorganic materials as the media for separation, we chose salts soluble in water with melting points higher than 700°C (including chlorides, sulfides and carbonates of Na, K and Ca) as the separating media. The salt powders were ball milled for more than 24 h to reach a particle size smaller than 20 μm before they were mixed with fcc FePt nanoparticles.

The fcc FePt nanoparticles with different sizes and shapes were synthesized by standard airless techniques in an argon atmosphere with adjustable synthesis parameters [1, 18–20]. The weight ratios of the salts to the fcc nanoparticles were varied. In the case of NaCl, ratios including 1 : 1, 2 : 1, 4 : 1, 8 : 1, 20 : 1, 30 : 1, 40 : 1 and 100 : 1 were tested. The mixtures were then annealed at temperatures ranging from 600°C to 700°C for 2–4 h under a neutral or reducing atmosphere (e.g. 'forming gas' with 95% Ar + 5% H$_2$). After annealing, the salts were removed from the samples by washing the mixtures in de-ionized water followed by centrifugation. The water was decanted from the centrifuge tube and then the previous step was repeated to ensure that the salts were completely removed from the samples. The remaining particles were then rinsed with acetone and centrifuged again. Dispersions of the fct FePt nanoparticles were eventually obtained in an organic solvent such as ethanol. Surfactants were not required to assist the dispersion.

Transmission electron microscopy (TEM), powder x-ray diffraction (XRD), inductively coupled plasma–optical emission spectroscopy (ICP–OES) and magnetization measurements were used to characterize the FePt nanoparticles before and after the salt-matrix heat treatments. A laser particle size analyzer was also used to check the particle size. The magnetic hysteresis measurements were carried out using a superconducting quantum interference device (SQUID) magnetometer with a field strength up to 7 T at different temperatures for the fct particles embedded in hardened epoxy or in frozen alcohol with and without the magnetic field alignment.

Among all the tested salts, it was found that NaCl gave the best results because of its high stability at annealing temperatures and high solubility in water. It was also the most economic choice in view of its availability. NaCl powder from a supermarket was tested and good monodisperse fct nanoparticles were obtained.

3. Results and discussions

Figure 1 shows XRD patterns of the annealed FePt nanoparticles in a NaCl matrix under different conditions. It can be seen clearly that well defined (001) and (110) peaks for fct FePt appear in samples annealed at 700°C for 2 h in forming gas. Diffraction peaks associated with NaCl or any other phases were not found in the XRD patterns, which indicate a minimal contamination by the salt during the annealing. ICP analysis confirmed a low level of Na contamination of 0.099% (wt/wt basis) and an average particle composition of Fe$_{52}$Pt$_{48}$.

The magnetization values of the salt-matrix annealed FePt nanoparticles were measured to check if any deterioration was caused by the contamination from the salt matrix during annealing or from water exposure during washing. For the recovered particles of 15 nm with salt to particle ratio of 40 : 1, for instance, the magnetization values at 7 T at room temperature (which are considered to be close to the saturation magnetization) are as follows: annealed at 600°C for 2 h, 733.5 emu cm^{-3}; 700°C, 2 h, 744 emu cm^{-3}; 700°C, 4 h, 841.5 emu cm^{-3}. These magnetization values are comparable to FePt particles annealed under the same conditions without salt. It is seen that the magnetization
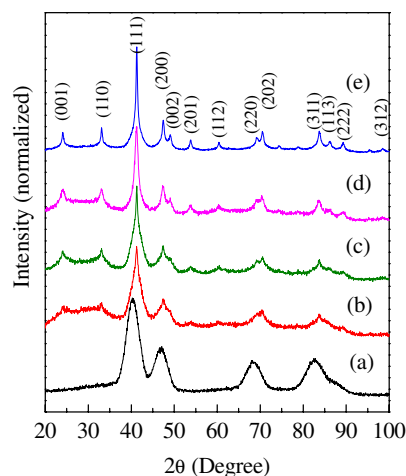

Figure 1. XRD patterns of the FePt nanoparticles. (a) The as-synthesized 4 nm FePt particles, (b) particle annealed at 600°C for 2 h with NaCl : FePt ratio 40 : 1, (c) at 700°C for 2 h with the ratio 1 : 40, (d) 700°C for 4 h with the ratio 100 : 1 and (e) 700°C for 4 h with the ratio 40 : 1. The diffraction patterns were collected with a Philips PW 1710 diffractometer with Cu Kα radiation (wave length $\lambda = 1.54056$ Å).

values increase with the annealing time and temperature, indicating a phase-transition (from disordered fcc to ordered fct structure) that resulted in an increase in magnetization. The higher the degree of the chemical order, the higher is the magnetization. A completely ordered fct bulk phase possesses very high saturation magnetization (1140 emu cm^{-3} at room temperature [21]). The relatively low magnetization values at 7 T of the nanoparticles, even after sufficient annealing, may be attributed to the reduced magnetic moment of the surface atoms of the nanoparticles and the fact that the 7 T field is not enough to reach the saturation.

The morphology of the salt-matrix annealed nanoparticles was closely monitored by TEM observations and a laser particle-size analyser. It was found that the annealed particles are easier to aggregate than the fcc particles because of the magnetic attraction force between the fct particles. This kind of aggregation can be re-dispersed by ultra-sonic vibration. Monodispersed nanoparticles can still be observed if the particles are properly deposited on TEM observation grids. Figure 2 shows images of the particles annealed at 700°C for 2 h. It can be seen clearly that this methodology has successfully prevented the particles with sizes ranging from 4 to 15 nm from sintering and growing at 700°C, which is high enough for a complete phase transformation from the fcc to the fct structure.

It has been found that the higher the salt to particle ratio, the lesser is the sintering. When the ratio is lower than 20 : 1, monodisperse fct nanoparticles cannot be obtained from heat treatments at 700°C for 2 h. Lower salt ratios give significant particle sintering and agglomeration. Annealing at higher temperatures and extended time should be accompanied by higher salt to FePt ratio in order to avoid sintering. From our experimental observations, the salt particle size has no significant effect on the annealing and the presence of salts has not altered the fcc to fct transition temperature.

From figures 2(b) and (d) it can be seen that most of the 8 nm particles have cubic or rectangular shapes, like their
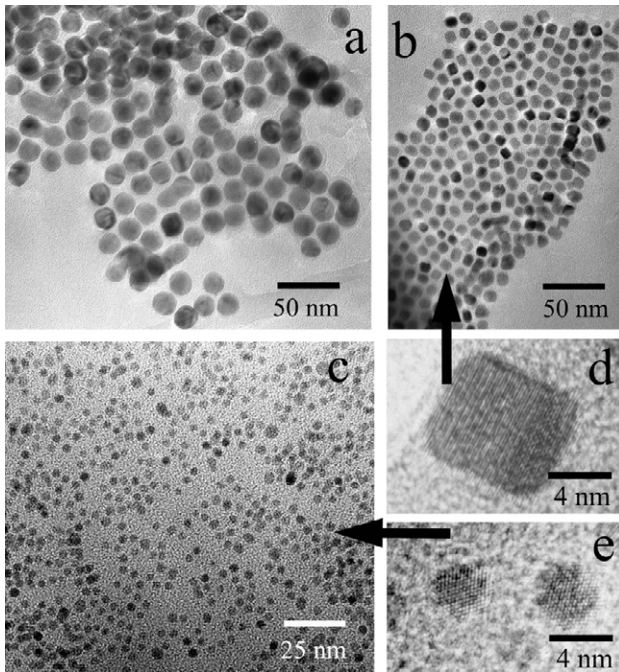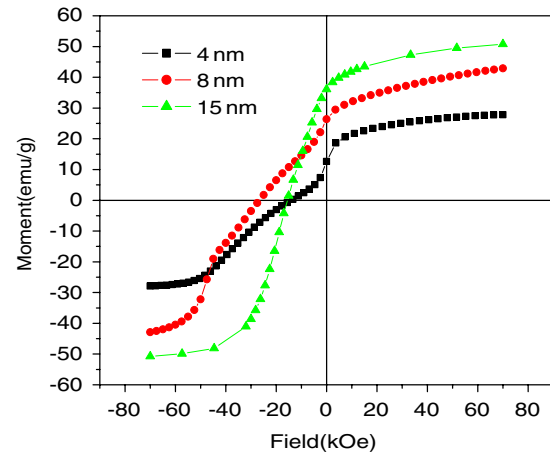
Figure 2. TEM images of salt-matrix annealed fct FePt particles annealed at 700°C for 2 h. (*a*) 15 nm with NaCl : FePt ratio of 100 : 1; (*b*) 8 nm with the ratio of 40 : 1; (*c*) 4 nm with the ratio of 40 : 1; (*d*) and (*e*) are the high resolution TEM images for (*b*) and (*c*), respectively.

Figure 3. Demagnetization curves of the annealed fct FePt nanoparticles with 4, 8 and 15 nm particle size. The annealing was performed in NaCl matrix at 700°C for 4 h in forming gas. The ratio FePt : NaCl = 1 : 100. The particles were embedded in epoxy.

Figure 4. Demagnetization curves of the aligned and non-aligned fct particles. The curves were measured at 10 K from the aligned 8 nm particles and the randomly aligned particles in frozen alcohol. The particles were annealed at 700°C for 4 h.

precursors before the annealing, indicating that nanoparticle shapes can be retained with this heat treatment technique. This technique can therefore, be readily applied to heat treatments of nanorods, nanowires and other isolated micro- and nanostructures as long as they can be mixed with salt powders and salt contamination can be avoided.

The major reason for the great interest in FePt nanoparticles is that fct FePt phase has very high magnetic anisotropy and therefore, fct FePt nanoparticles should have high coercivity as long as their size is above the superparamagnetic critical dimension. The annealed particles were mixed with epoxy and aligned in a magnetic field of 7 T. After the epoxy dried, the magnetization loops were measured with a SQUID magnetometer in different directions. The curves in figure 3 were measured along the alignment direction. Not surprisingly, the particles exhibited giant coercivity, up to 30 kOe at room temperature (see figure 3). In all the cases of the annealed particles, when the XRD patterns showed the fct structure, coercivity values of the isolated particles in epoxy were normally above 15 kOe at room temperature. It is interesting to note that the 8 nm particles have higher coercivity than the rest. We attribute this to the different shapes (cubic and rectangular) of the 8 nm particles. From figure 3 it can also be seen that the demagnetization curves of the 4 and 8 nm particles show kinks with relatively low saturation magnetizations, indicating a two-phase magnetization behaviour, which may be related to particle-size dependence of the phase-transition and is worth further investigation.

It was supposed that the fct particles with magnetocrystalline anisotropy should be aligned in a magnetic field and therefore, the hardened epoxy specimens could give different magnetization curves in different directions. However, it was
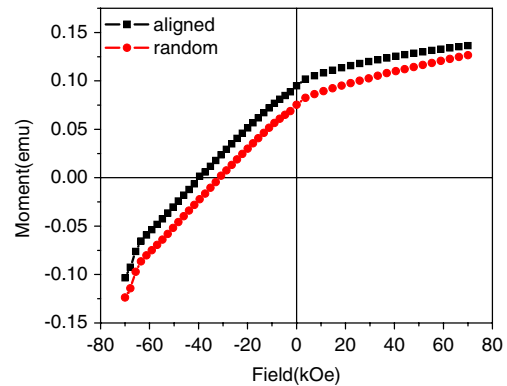
puzzling that no obvious difference could be found in the magnetization curves measured in the parallel and perpendicular directions. One possible reason for this phenomenon is that the fct particles (each of them is a small permanent magnet) attract each other to form large aggregations, which makes the rotation of individual particles difficult. Another reason may be that it is difficult to rotate the very fine nanoparticles with 7 T field in epoxy because of the friction. The high viscosity of epoxy and the huge surface area of the nanoparticles can make the friction extremely high. Alignment with higher magnetic field may be needed.

To reduce the friction, the particles were aligned in alcohol and water in a magnetic field of 7 T. The specimens were cooled down in the magnetic field, from room temperature at which alcohol and water are liquids, to temperatures below the ice points for alcohol and water, and then the demagnetization curves were measured. These curves were then compared with the curves measured for the samples cooled without the magnetic field (randomly aligned particles). Figure 4 shows the demagnetizing curves measured from the aligned particles and the random particles in frozen alcohol at 10 K. A significant difference has been found, although we were not able to
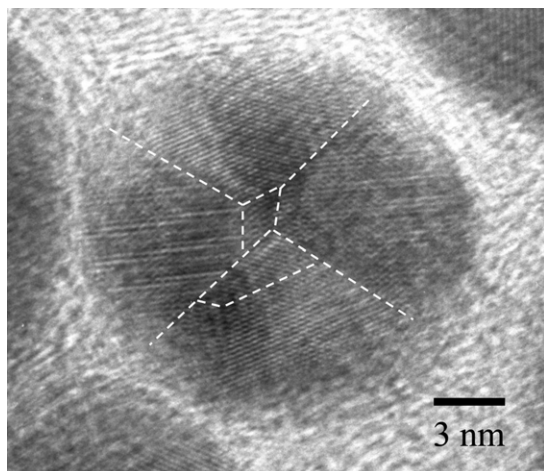
Figure 5. HRTEM image of an annealed fct FePt nanoparticle showing the polycrystalline morphology.

saturate the magnetization with 7 T magnetic field at 10 K. No kinks were observed in these minor-loop curves.

Another reason for the difficulty in aligning the nanoparticles is associated with an observation of the polycrystalline feature of the annealed fct particles. Figure 5 shows an example of an annealed nanoparticle with a high resolution TEM image. In the case of large sized particles (15 nm), polycrystalline particles comprise of more than 50% of the annealed particles, by a rough estimation.

In the case of polycrystalline nanoparticles, the domain-grain relationship can be complicated and the magnetization reversal cannot be described in a simple model. An extended understanding of this issue is on our wish list.

4. Conclusions

Although more work is needed to produce aligned nanostructured magnetic assemblies or bulks, our salt matrix annealing methodology reported here has a marked availability of the building blocks of highly anisotropic fct FePt nanoparticles. The direct application of fully converted fct FePt nanoparticles in magnetic-recording media and biomedical experiments are possible now. Based on a simple and economic processing feasible for industrial scale-up production, this technique can also be applied to the production of other isolated material structures where heat treatment, but not sintering, is required.

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