Reducing the ordering temperature of FePt nanoparticles by Cu additive and alternate reduction method

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(FePt)₈₅Cu₁₅ nanoparticles were successfully prepared by alternate reduction of metal salts in aqueous medium. Detailed investigations on the correlation between the magnetic and structural properties of these nanoparticles are presented as a function of annealing temperature. Both the X-ray diffraction patterns and the magnetic hysteresis loop measurements show the existence of L1₀-FePt phase at a relative low annealing temperature. It is proved that the Cu additive and alternate reduction are very effective methods in reducing the ordering temperature of FePt nanoparticles.

Keywords: L1₀ phase; low ordering temperature; Cu additive; alternate reduction method.

1. Introduction

The magnetic FePt and CoPt nanoparticles have attracted considerable attention in recent years, owing to the extraordinary high magnetocrystalline anisotropy ($K_u \sim 7 \times 10^6$ J/m³) in the ordered face-centered tetragonal phase (L1₀ phase) and other excellent physicochemical properties of the material, which have been investigated for various applications such as ultra-high density magnetic recording media, exchange-coupled nanocomposite magnets, biomedicines, biomedical applications and as a catalyst.^{1–8} The FePt nanometer materials can be synthesized by vacuum deposition techniques such as sputtering,^{9,10} chemical vapor deposition¹¹ and molecular beam epitaxy,^{12,13} etc. In addition, various chemical methods to control the size and shape of nanoparticles have also been used to synthesize FePt nanoparticles, such as the electrochemical method,^{14,15} coreduction method^{1,16–18} etc.

As-synthesized FePt nanoparticles are reported to have a chemically disordered face center cubic (FCC) phase and reveal superparamagnetic behavior. In the synthesis of L1₀-FePt nanoparticles, a high temperature treatment of about 500°C is necessary to transform the FCC phase into the L1₀ phase. However, annealing at higher temperature induces complete decomposition of the protective layer surrounding the surface of each particle and consequently leads to an undesirable aggregation. Recently, various methods have been attempted to reduce the FePt phase transition temperature. Addition of a third nonmagnetic element, such as Ag,¹⁹ Au,^{20,21} or Sb²² into FePt chemically synthesized nanoparticles,

has lowered the FCC to L1₀ transformation temperature. Moreover, introduction of Cu^{23,24} into FePt synthesized alloy or thin film has also been considered to reduce the ordering temperature. Encouraged by the results obtained in our previous communication on the stabilization of L1₀-FePt, continuous investigation on the FePt by a new synthesis method would be explored.

Recently, CoPt nanoparticles were produced in aqueous medium using hydrazine as a reducing agent.²⁵ The coercivity of CoPt nanoparticles was 2 kOe after annealing at 500°C. In the present paper, we present the synthesis of (FePt)₈₅Cu₁₅ nanoparticles by alternate reduction method and Cu additive. A detailed analysis of the sample structures obtained from the X-ray diffraction (XRD) and transmission electron micrograph (TEM) has been presented. The particles are nearly spherical shaped with a few nanometers in diameter. By the addition of Cu and alternate reduction, FePt nanoparticles annealed at 400°C have a very high coercivity of 4.43 kOe. FePt nanoparticles have been revealed totally L1₀ phase with a 10.9 kOe coercive field after being annealed at 600°C.

2. Experimental

(FePt)₈₅Cu₁₅ nanoparticles were synthesized by alternate reduction of chloroplatinic acid (H₂PtCl₆·6H₂O), ferric chloride (FeCl₃·6H₂O) and copper dichloride (CuCl₂·2H₂O) with diamide hydrate (N₂H₄·H₂O) as a reducing agent.

Acetyl trimethyl ammonium bromide (CTAB) was used as a surfactant in order to obtain well-dispersed nanoparticles. A 250 mL three-necked round bottom flask was equipped with magnetic stirring and argon atmosphere. The experiment was carried out under the blanket of argon atmosphere in order to avoid oxidation. CTAB (0.704 g) was firstly added into the flask, and heated up to 70°C. Then, 2 ml $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution and excessive amount of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added into the flask. After stirring for two hours, a black solution is obtained, indicating the complete reduction and formation of Pt nanoparticles as nuclei. The black precipitation was cleaned by distilled water to obtain the Pt nuclei. The Pt nuclei, 0.704 g CTAB, 2 ml $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2 ml $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solutions were added into the flask, mixed evenly by ultrasonic. Excessive amount of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added into the three flasks. After stirring for two hours, the precipitation was extracted and cleaned by distilled water. This step is a reduction of ferric chloride and copper dichloride to metallic iron and copper. It is hoped that the metallic iron and copper can be coated onto the Pt nuclei. Repeat the above experimental steps, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ which are alternately reduced with diamide hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), and Pt, Fe and Cu can be alternately coated over the nuclei.

The as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles were subjected to heat treatments at 200°C, 350°C, 400°C and 600°C for 10 h by using vacuum tube type high temperature sintering furnace (GSL-1400X). The annealing process was performed under the presence of high purity forming gas ($\text{Ar}+5\%\text{H}_2$) to avoid oxidation and assist further reduction. These samples were used for structural and magnetic investigations.

XRD analysis in the 2θ range 10° – 80° was performed to analyze the structure. The hysteresis loop at room temperature was measured by vibrating sample magnetometer (VSM). TEM was used to determine the size, shape and the existence of L_{10} phase of the nanoparticles dispersed on the copper grid.

3. Results and Discussion

The XRD patterns for the as-prepared sample and samples annealed at different temperatures were shown in Fig. 1. The as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ sample shows broad (111) peak at 41.56° , (200) peak at 47.4° and (220) peak at 68.9° . The appearance of the characteristic peaks shows that the as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ sample is FCC phase. For the sample annealed at 600°C, two distinguishable peaks at 24.2° and 33.1° corresponding to the (001) and (110) planes are observed, which is a clear indication of the existence of L_{10} phase. In other words, when annealed at 600°C, a transition from FCC phase to L_{10} phase occurs. Moreover, the (111) peak is more obvious and sharper after 600°C annealing, it migrates to big angle direction. It can be deduced that

Fig. 1. XRD patterns of the as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles sample and samples annealed at different temperatures.

the lattice constant changes in the phase transition and the aggregation of the nanoparticles occurs in the high temperature treatment process. For the sample annealed at 400°C, the (111) peak also migrates to larger angle, but the (001) and (110) characteristic diffraction peaks of L_{10} phase cannot be clearly seen. Hence, we cannot come to the conclusion of the phase transformation from FCC to L_{10} caused by 400°C annealing.

TEM was used to further investigate the phase transition and grain size. A spherical morphology for the as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles can be clearly seen in Figs. 2(a), 2(b) and 2(c). It is obvious that $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles were well monodisperse and the average particle size is about 8 nm. The corresponding SAED image of as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles shown in Fig. 2(d) gives the (111), (200) and (220) planes, which is the characteristic peak of FCC phase.

When annealing at 400°C, particles are also monodisperse, as shown in Fig. 3(a). The average particle size is similar to that of the as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles. The corresponding SAED pattern show planes of (111) and (200), which is prominently matching the analysis of XRD. The corresponding SAED in Fig. 3(b) shows that the FCC phase of particles are retained with the enhancement in the crystallinity. The (001) planes are not obviously the same as the XRD analysis.

The average particle size is about 70 nm after annealing at 600°C as shown in Figs. 4(a), 4(b) and 4(c). It can be clearly seen that serious agglomeration occurs. The particles are dispersed with aggregation after high temperature annealing, which is a common failure in almost all the FePt nanoparticles synthesized in aqueous medium. The corresponding SAED pattern of $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticle shows (110) and (001) plane of FePt in Fig. 4(d). According to the above analysis, the particles have been completely translated into L_{10} -FePt nanoparticles when annealed at 600°C.

Fig. 2. (a), (b), (c) TEM images of as-prepared (FePt)₈₅Cu₁₅ nanoparticle and (d) the corresponding SAED pattern.

Fig. 3. (a) TEM image of (FePt)₈₅Cu₁₅ sample annealed at 400°C and (b) the corresponding SAED pattern.

Fig. 4. (a), (b), (c) TEM images of $(\text{FePt})_{85}\text{Cu}_{15}$ sample annealed at 600°C and (d) the corresponding SAED pattern.

The M–H loop of the as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles was shown in Fig. 5. The as-prepared sample with FCC phase exhibits hysteresis loop with strong superparamagnetic properties, which is in accordance with the XRD and TEM analysis. The as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ sample exhibits a small coercive field of about 26.8 Oe.

The magnetic behavior of FePt nanoparticles were investigated as a function of annealing temperature, as shown in Fig. 5. The $(\text{FePt})_{85}\text{Cu}_{15}$ sample annealed at 200°C shows a coercive field of 28.3 Oe which is nearly the same as the as-prepared $(\text{FePt})_{85}\text{Cu}_{15}$ nanoparticles. After annealing at 350°C , coercivity field is enlarged, and the phase of few particles transform from FCC to L_{10} . The hysteresis loop of the sample annealed at 400°C exhibits a high coercivity of 4.43 kOe. The hysteresis loop also shows a small shoulder indicating the coexistence of both soft and hard phase as a result of an incomplete phase transition. Obviously, alternate reduction method and the addition of Cu are very effective

ways for reducing the ordering temperature. There is a marked increase in coercivity to 10.9 kOe of the sample annealed at 600°C . The hysteresis loop at 600°C shows a perfect loop suggesting the complete conversion from FCC phase to L_{10} phase. The hysteresis loop measurements clearly reveal that, with increase in annealing temperature, there is a gradual transformation from the FCC phase to L_{10} phase with an intermediate mixed phase. This transformation occurs at 400°C .

A lower ordering temperature of FePt to 400°C has been obtained in the present study. The reason for the decrease in ordering temperature lies in the synthesized method. The FePt sample was synthesized by alternate reduction and Cu additive. In a conventional synthesis process, iron salt, platinum salt and surfactant are well mixed and then coreduced, giving rise to a total disorder of the iron and platinum atoms distribution. In our experiment, Pt nuclei are firstly formed from the reduction of platinum salt. Then Fe–Cu atoms and Pt atoms will be coated onto the nuclei alternately by the

Fig. 5. M-H loops of the (FePt)₈₅Cu₁₅ nanoparticles annealed at 200°C, 350°C and 400°C and 600°C.

coreduction of the nuclei and metal salts. This implies that Fe atoms and Pt atoms were independently produced at initial reaction stage, so most likely, the as-synthesized particles consist of layered Fe, Cu, Pt and possible oxides. The increase of defects and boundaries in nanoparticles cause the increase of a driving force of the phase transition, which can reduce the ordering temperature. The magnetic analysis clearly shows that, the phase transition of the (FePt)₈₅Cu₁₅ partly occurs at 400°C with no aggregation of particles in the TEM image. In spite of the total phase transition of the (FePt)₈₅Cu₁₅ observed when annealed at 600°C, the aggregation of particles cannot be well controlled. Preventing the particles from aggregation is also essential for applications. Achieving monodispersed L1₀-FePt nanoparticles at 400°C is under process by longer time annealing.

4. Conclusions

Monodisperse (FePt)₈₅Cu₁₅ nanoparticles were successfully synthesized by the alternate reduction method. The average particle size is 8 nm. The VSM measurements show high coercivity of (FePt)₈₅Cu₁₅ sample of 4.43 kOe after 400°C annealing and 10.9 kOe after 600°C annealing. Due to the addition of Cu and the alternate reduction method, the phase transition temperature was reduced from the conventional annealing temperature of about 500°C to 400°C with no obvious aggregation of particles. Hence, the alternate reduction method and the addition of Cu element can be very effective ways in reducing the ordering temperature of FePt nanoparticles. It should be pointed out that the alternate reduction method is not suitable for high temperature synthesis, but only for moderate environment synthesis.

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