Bulk FePt-based nanocomposite magnets with enhanced exchange coupling

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(Received 19 March 2007; accepted 2 June 2007; published online 23 July 2007)

High density bulk FePt/Fe3Pt nanocomposite magnets have been prepared by high-pressure warm compaction of chemically synthesized FePt and Fe3O4 nanoparticles. It is found that the density increases with the compaction pressure and temperature. Density of the bulk samples up to 95% theoretical value has been obtained while the nanostructured morphology is retained. It is also observed that a high pressure expedites the FePt phase transition from the disordered face-centered-cubic structure to the L10 structure, leading to the phase transition temperature in the compacts one hundred degrees lower than usual. This phase transition in turn facilitates the consolidation of the compacts. Magnetic characterizations showed that interphase exchange coupling is enhanced upon the compaction. Post-annealing of the compacts results in further improved magnetic performance of the compacts owing to interface modification. Energy products up to 16.3 MG Oe of the isotropic bulk nanocomposite magnets have been achieved, which is significantly higher than the theoretical limit for fully dense single-phase FePt magnets. © 2007 American Institute of Physics.

DOI: 10.1063/1.2756619

I. INTRODUCTION

Exchange-coupled hard/soft nanocomposite magnets have attracted great interest in the last decade because of their potential in achieving giant energy product (BH)max that may be as large as 100 MG Oe. Effective interphase magnetic exchange coupling in the nanocomposites can be achieved if dimensions of the soft-phase components are not larger than a nanoscale critical length. The grain size in nanocomposite magnets fabricated by conventional top-down methods, including mechanical alloying and rapid quenching, usually has a wide distribution, and can hardly be controlled below the critical length. An alternative bottom-up approach therefore is necessary to fabricate nanocomposite magnets with controllable nanoscale morphology. Recently, magnetic FePt nanoparticles synthesized by chemical solution methods have aroused significant attention because of their very small particle size and size distribution, which makes them ideal building blocks for exchange-coupled nanocomposite bulk magnets. The biggest challenge for the bottom-up approach is how to produce bulk nanostructured magnets without losing the homogenous nanoscale morphology. Conventional compaction and condensation techniques cannot be applied for nanoparticles since those techniques require extensive heat treatments which lead to excessive grain growth. To date, there have been very limited data reported on direct compaction of intermetallic nanoparticles, especially for nanoparticles with size down to several nanometers. Recent attempts to fabricate bulk nanostructured magnets by using unconventional compaction techniques including plasma sintering and dynamic compaction have resulted limited success. Bulk samples with density up to 80% theoretical value have been obtained. The challenge remains in producing bulk nanostructured magnets with density close to theoretical values.

On the other hand, the as-synthesized FePt nanoparticles have the disordered face-centered cubic (fcc) structure with vanishing magnetocrystalline anisotropy. High temperature annealing (above 600 °C) is necessary to obtain the ordered L10 structure with very high magnetocrystalline anisotropy for hard magnetic applications. The challenge is how to avoid excessive particle or grain growth at such high temperatures. Adding third elements is one possibility to reduce the ordering temperature, while it inevitably decreases the magnetization which is harmful for applications as permanent magnets. Since the high pressure may reduce the phase transition temperature, the high-pressure warm compaction is therefore considered to be applicable to fabrication of nanoparticle based composite magnets.

High-pressure warm compaction is one of the advanced compaction techniques in powder metallurgy and has been widely used in automobile parts manufacturing in the past decade. This technique is established on the knowledge that metallic powders have better plasticity and compressibility at elevated temperatures and therefore are easier to be deformed to form high density bulks under a certain pressure, compared with cold pressing. Unlike hot pressing,
warm compaction is performed at modest temperatures at which the metallic powders are chemically stable and no excessive grain growth occurs.

In this work, we report our recent results in preparation and characterization of bulk FePt/Fe3Pt nanocomposite magnets by compacting chemically synthesized FePt and Fe3O4 nanoparticles at modest temperatures.

II. EXPERIMENTAL

The nanoparticles were synthesized by standard airless chemical solution procedures.13,26,27 The FePt with fcc structure and Fe3O4 nanoparticles were mixed at a mass ratio of 8:1 in a solution before centrifugation. The dried nanoparticles were heated under Ar atmosphere at 350 °C for 1 h to remove surfactants. The powders were then compacted with a warm-compaction press under pressure of 2.5 or 3.8 GPa for 10 min at temperatures ranging from room temperature (about 20 °C) to 600 °C. The obtained bulk samples had dimensions φ6 mm × 1.5 mm and φ3 mm × 1.2 mm for the compaction pressures of 2.5 and 3.8 GPa, respectively. For comparison, we also compacted 15 nm L10 FePt nanoparticles prepared by the salt-matrix annealing technique16,28 at 2.5 GPa pressure. The Archimedes method was employed for measurements of bulk sample density. The morphology and crystalline structure were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and x-ray diffraction (XRD) using Cu Kα radiation. The composition of the compacted samples were checked by energy dispersive x-ray (EDX) analysis in SEM. Magnetic properties were measured with superconducting quantum interference device magnetometer with a maximum applied field of 70 kOe.

III. RESULTS AND DISCUSSIONS

A. Density

It is known that the limit for density ρp of a randomly packed particle system is only 64% if no deformation is involved.29 To obtain a higher ρp, it is necessary to realize plastic deformation of the particles. For nanoparticles, the deformation will not be as for large particles because of the reduced dislocations in the particles, which explains low density values obtained in nanoparticle compacts. Figure 1 shows the dependence of ρp of the bulk samples on the compaction temperature (Tcp) under different pressures. One can see that the density increased monotonously with compaction temperature for both fcc and L10 particle compacts. The samples prepared at pressure 3.8 GPa and Tcp of 600 °C has the highest density (13.8 g/cm3) which is about 95% of the full density value (14.5 g/cm3 for the FePt/Fe3Pt composite with 15% volume fraction of Fe3Pt phase). Such high density is a result of a significant plastic deformation of the nanoparticles at the applied high pressure. A linear increase in the density can be observed for the L10 particles in the whole studied temperature range and for the fcc particles in the temperature range from 20 to about 400 °C. This may be explained by the fact that the yield strength of metallic FePt materials decreases linearly with temperature in the region between 20 and 800 °C (Ref. 30) and an effective lubrication mechanism can occur in the heated powders.19 However, this linear increase in density did not lead to full densification, even one extrapolate the curve to a high temperature.

Figure 1 shows that for the fcc nanoparticles, the dependence of ρp on Tcp became steeper when Tcp ≥ 400 °C. This nonlinear behavior may be related to the phase transition from the disordered fcc to the ordered L10 structure during which atoms are activated and become more mobile. The enhanced atomic diffusion promoted densification of the compacts and resulted in high density. On the other hand, the phase transition may also accelerate the formation of Fe3Pt phase in the FePt-Fe3O4 nanoparticle system.14 Approximately 15% volume fraction of Fe3Pt phase was determined by using the method of Rietveld refinement of the XRD pattern which will be discussed later.

SEM analysis was performed on the fracture surfaces of the compacts to characterize morphological changes in the compacted samples. Figure 2 shows the typical SEM images of the bulk samples compacted at 20, 400, and 600 °C. The 20 °C-compacted samples are quite porous. With increasing Tcp to 400 °C, it is interesting to find that stripes with thickness around 10–20 μm were formed. However, some small holes were still found in the layers. Compacting at 600 °C led to very large and homogenous areas (>150 μm) in the compact and thus the high density. The SEM morphology change agrees with the dependence of density on compacted temperature as shown in Fig. 1.

B. Phase transition

As mentioned earlier, the rapidly increased density at the compaction temperature higher than 400 °C may be related to the phase transition of FePt component from fcc structure.
to the $L1_0$ structure. To study the phase transition, we performed XRD measurement of the 20, 400, and 600 °C-compact samples and the patterns are shown in Fig. 3. It can be seen that the 20 °C-compact mainly consists of fcc FePt and Fe$_3$O$_4$ phases. The compaction at 400 °C led to the phase transition of FePt component from fcc to $L1_0$ structure while Fe$_3$O$_4$ was still existing. With increasing $T_{cp}$ to 600 °C, the FePt phase is of $L1_0$ structure and the Fe$_3$O$_4$ disappeared. The quantitative analysis of the phase content can be made approximately by using the method of the Rietveld refinement on XRD patterns.

As an example, the Rietveld refinement data of the 600 °C compact is also included for the 400 °C-compacted sample. The symbol (●) and full line represent the observed and calculated x-ray diffraction profiles, respectively. The vertical bars represent the Bragg reflection positions of the observed phases (from top to bottom: $L1_0$, FePt and Fe$_3$Pt). The difference curve is plotted in the bottom.

FIG. 3. (Color online) XRD patterns of the bulk samples compacted at (a) 20, (b) 400, and (c) 600 °C. The Rietveld refinement data are also included in (c) for the 600 °C-compacted sample. The symbol (○) and full line represent the observed and calculated x-ray diffraction profiles, respectively. The vertical bars represent the Bragg reflection positions of the observed phases (from top to bottom: $L1_0$, FePt and Fe$_3$Pt). The difference curve is plotted in the bottom.

FIG. 4. (Color online) The dependence of $S$ on $T_{cp}$ for the bulks. For comparison, the dependence of $S$ on annealing temperature of the starting powder is also included for 10 min annealing.

The phase transition is also confirmed by the dependence of magnetic properties on $T_{cp}$. Figure 5 shows the dependence of saturation magnetization $M_s$ (measured in an applied field of 7 T) and coercivity $H_c$ on $T_{cp}$. The samples compacted at relatively low temperatures ($T_{cp}<400$ °C) showed nearly zero coercivity, while the 400 °C-compacted sample gave $H_c$ of 10 kOe. The drastic increase in coercivity originated from the formation of the $L1_0$ phase with high magnetocrystalline anisotropy. Since a higher $T_{cp}$ led to a higher density of the compacts and thus a reduced surface effect, the $M_s$ value was increased from 850 to 1200.
970 emu/cm$^3$ with increasing $T_{cp}$ from 20 to 300 °C. However, the $M_s$ dropped to 800 emu/cm$^3$ at $T_{cp}=400$ °C, which can be attributed to the phase transition since the antiparallel alignment of the polarized Pt spins to the Fe spins in the $L1_0$ ordered FePt alloys and thus $M_s$ of the $L1_0$ phase is lower than that of the fcc phase. Similar results were reported in Ref. 41, where the $M_s$ decreased by about 30% from 1000 emu/cm$^3$ of the fcc phase to 670 emu/cm$^3$ of the $L1_0$ phase. Considering the FePt/Fe$_3$O$_4$ mass ratio of 8:1 in our samples, the decrease of $M_s$ should be 23% if the fcc phase is completely transferred to the $L1_0$ phase, which is in good agreement with the observed result. The further increase of $T_{cp}$ resulted in a fast increase of $M_s$, due to the decomposition of magnetite and the formation of Fe$_3$Pt phase during the compaction at relatively high temperature.

### C. Microstructural characteristics

To quantitatively determine the effect of warm compaction on the microstructure, x-ray diffraction line-broadening analysis was performed on the bulks. The grain size and retained strain were then determined using the Williamson–Hall analysis method. Figure 6 shows the dependence of grain size and microstrain on $T_{cp}$ for as-compacted samples. The grain size of the annealed samples and the compacted $L1_0$ nanoparticles are also given.

![Graph showing dependence of grain size and microstrain on $T_{cp}$](image)

**FIG. 6.** (Color online) The dependence of grain size and microstrain on $T_{cp}$ for as-compacted samples. The grain size of the annealed samples and the compacted $L1_0$ nanoparticles are also given.

The grain size of bulk samples with post-annealing (compacted under 2.5 GPa and annealed in forming gas at 500 °C for 1 h) was also included in Fig. 6 to illustrate the effect of heat treatment on the morphology. It is found that the annealing led to the grain growth from 6.5 to 16 nm for the 20 °C-compacted sample, while only from 22 to 25 nm for the 600 °C-compacted sample, implying that the phase transition is the main reason for the grain growth. This is also evidenced by the observation that grain size of the $L1_0$ nanoparticles was almost unchanged during the annealing. The compacts made by the 15 nm $L1_0$ nanoparticles showed no grain growth up to 600 °C (see Fig. 6). To confirm this observation, we heated the samples to 1000 °C for 1 h and found that the average grain size was just slightly increased to about 17 nm. The high stability of the $L1_0$ structured nanoparticles can be utilized for fabrication of bulk nanocomposite magnets with very fine and homogenous nanoscale morphology.

**FIG. 7.** TEM micrographs of bulk samples compacted at different temperatures. (a) 20, (b) 400, (c) 600 °C, and (d) SAED patterns at different temperatures.

![TEM micrographs of bulk samples](image)

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Figure 7 shows the bright field TEM images of the bulk samples prepared from fcc nanoparticles under 2.5 GPa pressure at 20, 400, and 600 °C. The selected area electron diffraction patterns [Fig. 7(d)] confirm the phase transition. The TEM images show that grain size increases with $T_{cp}$ as ex-
negative interpreted as a sign for magnetic exchange coupling and the demagnetization remanence and inset of Fig. 8 reflected by the shape of the hysteresis loops, as shown in the 400 °C-compacted samples with lower density. This is also exchange coupling in the compact compared to the 600 °C-compacted sample, indicating stronger exchange coupling in the 600 °C-compacted samples, post-annealing under forming gas.

D. Exchange coupling and magnetic properties

All the efforts in controlling grain size are made for the purpose to realize intergranular magnetic exchange coupling and thus to achieve high energy products. To study the magnetic interactions in the warm compaction-produced nano-composite magnets, the \( \delta m = m_r(H) - [1 - 2m_r(H)] \) measurements (Henkel plots) were performed.\(^{43-45} \) Here \( m_r \) is demagnetization remanence and \( m_r \) is isothermal magnetization remanence. Both of these values are normalized by the saturation remanence. Nonzero \( \delta m \) is caused by magnetic interactions between particles or grains. The positive \( \delta m \) is interpreted as a sign for magnetic exchange coupling and the negative \( \delta m \) is a sign of magnetic dipolar interaction. Figure 8(a) shows \( \delta m \) plots of 400 and 600 °C-compacted samples prepared from the fcc particles. The \( \delta m \) value for the 600 °C-compacted sample is positive and much higher than that for the 400 °C-compacted sample, indicating stronger exchange coupling in the compact compared to the 400 °C-compacted samples with lower density. This is also reflected by the shape of the hysteresis loops, as shown in the inset of Fig. 8(a). The remanence ratio \( (M_r/M_s) = 0.63 \) where \( M_r \) is the remanent magnetization of the 600 °C-compacted sample is higher than that of the 400 °C compacted (0.58), which is also consistent with the \( \delta m \) measurement. This effect is even more pronounced for the \( L_{10} \) particle samples. Figure 8(b) shows the Henkel plots for 15 nm \( L_{10} \) nanoparticles and their compacts. \( \delta m \) for them before compaction is a large negative value. After the compaction at 2.5 GPa and 200 °C, \( \delta m \) changed its sign to positive, indicating an inter-particle exchange interaction. Annealing of the compact at 1000 °C for 1 h led to further increase in \( \delta m \) value and thus an enhancement of the exchange coupling. As the annealing causes almost no obvious grain growth, the strong increase in \( \delta m \) can be attributed to improvement in interface conditions upon the high temperature annealing. This result is consistent with the results reported in Ref. 46. The inset in Fig. 8(b) gives the hysteresis loops of the \( L_{10} \) nanoparticles and its compacts. It shows that the enhanced exchange coupling significantly improves the squareness of the hysteresis loops and therefore the energy products. A (BH)\(_{\text{max}}\) about 15.6 MG Oe has been obtained based on the measurement from the real density.

The magnetic properties can be further improved by a post-annealing under forming gas (93%Ar+7%H\(_2\)) for 1 h. Figure 9 shows the effect of annealing temperature (\( T_a \)) on \( M_s \), \( H_c \), and (BH)\(_{\text{max}}\) of the 20, 400, and 600 °C compacts. As shown in Fig. 9(a), \( M_s \) of the 20 and 400 °C compacts increased significantly after the annealing. This was attributed to the decomposition of Fe\(_3\)O\(_4\) phase and the formation of Fe or Fe\(_3\)Pt with high magnetization in the reducing atmosphere. \( M_s \) value up to 1140 emu/cm\(^3\) can be obtained by post-annealing. However, it is found that \( M_s \) of the 600 °C-compacted sample had a very small change upon post-annealing. This may be due to the early formation of Fe\(_3\)Pt phase during the warm compaction as discussed early. For all the samples compacted at the three temperatures, high-temperature annealing (\( >600 \) °C) led to a decrease in \( M_s \), which may be related to the atomic diffusion between FePt and Fe\(_3\)Pt.\(^{12} \) As shown in Fig. 9(b), \( H_c \) of the 20 °C-compacted samples increases fast when \( T_a \) is higher than 450 °C which shows that the phase transition from fcc to \( L_{10} \) resulted in magnetic hardening. For the 400 and 600 °C-compacted samples, post-annealing did not improve the \( H_c \) since the phase transition had already happened during the warm compaction. In this case, high-temperature annealing led to an overgrowth in grain size and therefore deterioration in the magnetic properties. By optimizing the post-annealing parameters further improvement of the (BH)\(_{\text{max}}\) up to 16.3 MG Oe (based on the real density for

FIG. 8. (Color online) (a) \( \delta m \) plots of the samples compacted at 400 and 600 °C from the fcc nanoparticles. (b) \( \delta m \) plots of the separated \( L_{10} \) particles and samples compacted (at 2.5 GPa, 200 °C) from the \( L_{10} \) nanoparticles as well as the post-annealed bulk samples. The insets are the corresponding demagnetization curves.
Fig. 9. (Color online) The dependence of $M_s$, $H_c$, and $(BH)_{\text{max}}$ on the annealing temperature for 20, 400, and 600 °C-compacted samples.

600 °C compact) has been achieved which is significantly higher than the theoretical limit (13 MG Oe) for the single-phase isotropic FePt magnets.

IV. CONCLUSIONS

In summary, high density FePt/Fe$_3$Pt bulk nanocomposite magnets have been obtained by the warm compaction method. A density up to 95% of the full density has been achieved while the nanoscale morphology is retained. Effective exchange coupling in the high-density bulk samples is realized. It is found that the pressure expedites the fcc-$L_1_0$ phase transition. The phase transition temperature shifts to a temperature lower than 400 °C under 2.5 GPa pressure. The phase transition has a positive effect on consolidation of the compacts. It has also been observed that the $L_1_0$ nanoparticles have high stability during heat treatments. Followed by a proper post-annealing treatment, magnetic properties of bulk samples can be significantly improved. Our results show that warm compaction technique is promising for producing high performance bulk nanocomposite magnets for advanced applications.

ACKNOWLEDGMENTS

This work was supported by U.S. DoD/MURI Grant No. N00014-05-1-0497 and DARPA through USARO under Grant No. DAAD 19-03-1-0038. The work at University of Texas at Dallas was supported by the Robert A. Welch Foundation Grant No. AT-0029.

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