

2002

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J. Appl. Phys 91, 8816 (2002).

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Synthesis and magnetic properties of CoPt–poly(methylmethacrylate) nanostructured composite material

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We have prepared nanometer-sized CoPt particles dispersed in a poly(methyl methacrylate) (PMMA) matrix, as a novel nanostructured magnetic plastic, through a soft chemical processing route. In this work, CoPt nanoparticles were successfully synthesized from a solution phase reduction system in the presence of capping ligands and stabilizing agents at high temperature. The CoPt nanoparticles were annealed at 400 °C for 3 h, and were subsequently re-dispersed in methylmethacrylate (monomer). The polymerization was induced by a UV source and the hardness of final product was adjusted by varying the amount of monomeric cross-link agent. Annealed bare CoPt nanoparticles as a “core” material and CoPt–PMMA composite material were characterized by using energy dispersive spectroscopy, transmission electron microscopy, and x-ray diffraction, indicating that we are able to prepare CoPt nanoparticles with <10 nm in diameter (after annealing) by employing this high temperature colloidal processing method. Magnetic investigation of this CoPt–PMMA material indicates an intrinsic coercivity of 300 Oe at 300 K and 1665 Oe at 5 K. © 2002 American Institute of Physics. [DOI: 10.1063/1.1453329]

I. INTRODUCTION

Magnetic nanocomposites are an important class of advanced functional materials, and have attracted attention in recent years for magnetic applications such as high-density storage media. The search for new inorganic magnetic materials as “core components” in these composites demands particles with nanometer-scale size so that each particle can be considered as a single magnetic domain. In this article, we present a novel chemical route for fabricating quasimonodisperse CoPt nanoparticles at high temperature as well as CoPt–polymer composites. The magnetic properties of both the CoPt core material and composite material will be discussed.

II. EXPERIMENT

A. Chemicals

In this investigation, super hydride [LiB(C₂H₅)₃H, 1.0 M in tetrahydrofuran (THF)] was used as a reducing agent. Since THF has a low boiling point, it must be completely replaced by another solvent under inert gas before use.^{1–3} The starting materials also include oleic acid (90%), oleylamine (70%), cobalt (II) chloride (97.0%), dioctyl ether (99.0%), di(ethylene glycol) 2-ethylhexyl ether (98%, hereafter DEGEE), methylmethacrylate (99.0%, hereafter MMA), 2-hydroxyethyl methacrylate (>99.0%, hereafter HEMA), ethylene glycol dimethacrylate (98.0%, hereafter EGDA), 2,2-dimethoxy-2-phenylacetophenone (99.0%, hereafter “UV-initiator”), tributylphosphine (97.0%, hereafter TBP) and platinum (II) acetylacetonate [Pt(C₅H₇O₂)₂, >99.5%]. All of the chemicals were purchased from Aldrich with the exception of the platinum acetylacetonate, which was purchased from Alfa Aesar.

B. Synthetic procedure

Preparation of CoPt–polymer nanostructured composites consists of three steps: fabrication of CoPt seeds, synthesis of CoPt nanocrystals and *in situ* formation of magnetic nanocomposites. In the first step, 5 ml of dioctyl ether solution consisting of 0.7 mg of CoCl₂ + 1.2 mg of Pt(C₅H₇O₂)₂ + 50 μl of oleic acid in a 25 ml round bottle flask was heated to 200 °C under argon stream and 0.25 ml solution of super hydride in dioctyl ether (0.5 M) was injected. The mixture was vigorously stirred and kept at 280 °C for 20 min. In the second step, CoCl₂ (anhydrous, 0.1238 g), Pt(C₅H₇O₂)₂ (0.2140 g), oleic acid (0.25 ml), oleylamine (0.50 ml) and dioctyl ether (50 ml) were mixed in a three-neck round bottom flask under argon and the temperature was steadily increased (~5 °C/min). At 250 °C, 5 ml of super hydride in DEGEE (1.0 M) was injected into the flask containing the CoPt seed particles prepared in the first step (warning: gas bubbles will evolve from the hot solution). The black solution was stirred at 280 °C for an additional 40 min with a refluxing device. Finally, TBP (0.45 ml) was injected into the flask and the heating source was quickly removed. The system was allowed to cool to room temperature naturally under argon. As-prepared Co/Pt nanoparticles were collected by centrifugation, solvent washing and vacuum drying.^{1,4} The magnetic CoPt particles were then annealed at 400 °C for 3 h under argon. The annealed CoPt powder was re-dispersed into MMA assisted by ultrasonication for 30 min under argon atmosphere. Within a glovebox, this black homogenous suspension was subsequently transferred into an *in situ* polymerization system containing the following components: MMA (total), 2.6510 g; HEMA, 0.5754 g; EGDA, 0.9856 g; UV-initiator, 0.2003 g; annealed CoPt, 0.0502 g. Polymerization was initiated by UV light (365 nm, 100 W) and the sample was continuously irradiated for 60 min.

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C. Characterization

Morphology and composition of the annealed CoPt nanoparticles were characterized using transmission electron microscopy (TEM, JEOL 2010) and energy dispersive x-ray spectroscopy (EDS). Magnetic properties measurement and phase characterization of the nanostructured composites were conducted using a superconducting quantum interference device magnetometer (MPMS-5S Susceptometer from Quantum Design) and x-ray powder diffractometer (Cu $K\alpha$, Philips X'pert-systems), respectively.

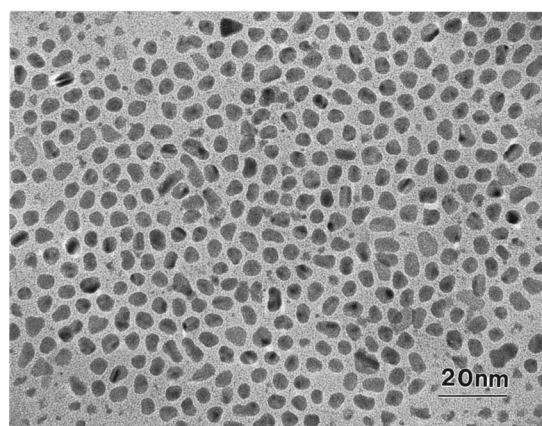
III. RESULTS AND DISCUSSION

A. Formation of nanoparticles and structural properties

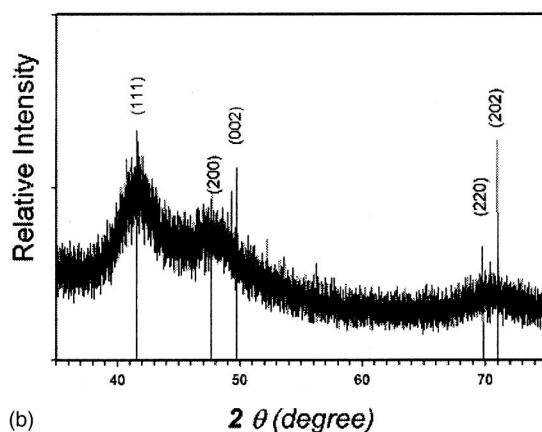
In this work, dioctyl ether as a high boiling point, non-polar organic solvent was chosen as a reaction medium. Cobalt salt and platinum salt with a molar ratio of 1.75:1 were dissolved in this organic phase, and reduced by super hydride at high temperature. A similar procedure was used by Sun *et al.* for preparing Co nanocrystals¹ and FePt nanocrystals.² In order to allow the nanoparticles to grow large enough, we used a small amount of DEGEE (DEGEE/dioctyl ether $\leq 1:10$) as the solvent medium of super hydride, not only because of the excellent solubility of DEGEE in dioctyl ether, but also due to its high boiling point. Nevertheless, a higher concentration of polar DEGEE will collapse this high temperature colloidal system. The as-prepared CoPt colloids were stabilized by a combination of organic ligands (oleic acid and oleyamine). The presence of CoPt seeds may help to form nanoparticles with better quality after the reduction as reported for Ag nanoparticles.⁵ In order to protect the as-prepared CoPt nanoparticles against possible agglomeration in later stage and to decrease the tendency of oxidation, we also introduce TBP, an excellent capping agent for Co-containing colloids.^{1,2,6} However, our results indicate that TBP limits the particle growth if it is introduced too early.

Using a light scattering technique the mean radius of unannealed CoPt particles was measured as 6.3 nm, and no agglomerate has been detected. Figure 1(a) is a TEM image, showing the morphology of CoPt nanoparticles annealed at 400 °C for 3 h. It reveals that the particles are virtually uniform in size and are elongated, not spherical. The size of particles covers a range from 4 to 7 nm in diameter. Nominal elemental analysis was also conducted using an energy dispersive analysis by x-ray (EDS) attachment on the same TEM instrument. Characteristic peaks of Co and Pt were present, and the average molar ratio of Co/Pt was determined as 46:54. To study phase development of the annealed CoPt nanoparticles, sample was also analyzed using x-ray powder diffraction (XRD) technique at room temperature. The XRD trace of the annealed CoPt particles, illustrated in Fig. 1(b), indicates that the CoPt phase is close to quasicubic crystal (tetragonal structure with $a = 3.803$, $c = 3.701$ and $C = 0.9732$) according to the standard ICDD pair distribution function (PDF) (Card No. 43-1358).

Due to the ultrafine size, the annealed CoPt particles could still be dispersed into MMA when assisted by ultrasonication. Polymerization was subsequently conducted by



(a)



(b)

FIG. 1. (a): Transmission electron micrograph of bare CoPt nanoparticles annealed at 400 °C for 3 h. (b): XRD trace of CoPt nanoparticles, annealed at 400 °C for 3 h.

adding the proper amount of co-monomer and cross-link agent as described above. The hardness of the final product can also be adjusted by varying the amount of monomeric cross-link agent.

B. Magnetic properties

The zero-field cooled (ZFC) and field cooled (FC) magnetization curves of the composite CoPt-poly(methylmethacrylate) (PMMA) are plotted in Fig. 2. Up to 350 K, we do not observe any blocking temperature (T_B) and the sample remains ferromagnetic to above room temperature. Our results here are different from a previous report in which the blocking temperature was determined as 140 K for 18 nm bare CoPt (spherical) particles synthesized in a room-temperature process.⁷ It is worth mentioning that the size of the CoPt particles in our sample is about 4–7 nm and, as mentioned above, the particles are not spherical. It is known that for a magnetic particle system with interaction, the T_B (temperature of maximum magnetization⁸) can be estimated by^{9,10}

$$T_B \approx (E_a + E_{\text{int}})/30k_B, \quad (1)$$

where E_a is the anisotropy energy and E_{int} inter-particle interaction energy. The small size of CoPt particles should give rise to the reduction of the energy barrier, which for the uniaxial symmetry is equal to KV (where K is the magnetic

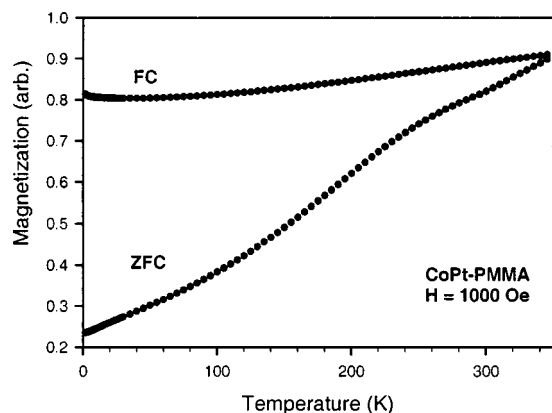


FIG. 2. ZFC and FC of composite CoPt-PMMA measured at the applied field of 1000 Oe.

anisotropy constant and V the particle volume), and hence reduces the blocking temperature. Another similar effect is the polymerization, which leads to the significantly weaker inter-particle interaction compared with the bare CoPt sample and hence decreases the energy barrier E_{int} ¹¹ and the blocking temperature as well. Instead of the size and polymerization effects, therefore, the higher blocking temperature in our sample may be attributed to the influence of particle morphology, i.e., the irregular shape, structural order-disorder difference¹² and the different synthetic technique as well, resulting in a different particle surface chemistry.

The hysteresis loops at 300 K of annealed CoPt sample before (a) and after (b) polymerization are plotted in Fig. 3. Up to the field measured of 5 T, the saturation moment is about $1.5\mu_B/\text{CoPt}$ at., which is significantly lower than that of 1.94 reported for stable CoPt film,¹³ and the reduced remanence of our sample, M_r/M_s , is about 0.2. The large difference between the saturation magnetization of our nanocrystals, M_s , and that of the stable thin film, is attributed to the strong interaction between the carbonyl residue of the coating agent and the Co atoms at the particle surface. This effect was calculated and observed for small Ni and NiPt clusters coated by Co ligands. Carbonyl ligands completely quench the magnetic moments of the Ni atoms at the cluster surface, leaving the inner core metal atoms unaffected.¹⁴

Our bare CoPt sample (after annealing) exhibits an intrinsic coercivity (H_c) of 260 Oe at 300 K. The CoPt sample dispersed in PMMA gives H_c of 300 Oe at 300 K, and 1665 Oe at 5 K. The lower value of H_c for the bare CoPt sample compared with the polymerized composite is interesting. The stronger inter-particle interaction in the unpolymerized sample may act to reduce the coercivity or¹⁵ it may be due to the difference in the surface chemistry between the polymerized and unpolymerized samples. Moreover, it has been reported that CoPt can be crystallized in two different phases: the (magnetically soft) disordered fcc structure and the (magnetically hard) ordered fct structure. From the x-ray measurement, it is difficult to distinguish between fcc CoPt and fct CoPt phases as their XRD patterns are very similar and all

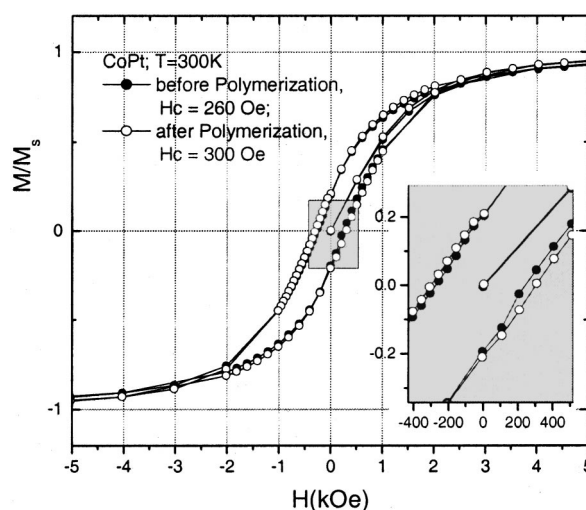


FIG. 3. Hysteresis loop measured at 300 K of annealed CoPt nanoparticles: (●) before polymerization and (○) after polymerization.

the peaks are considerably broadened due to very small particle sizes.¹⁶ These two different phases, however, can be distinguished from the magnetic measurements. In our CoPt-PMMA sample, the small value of H_c , i.e., 260 Oe (before polymerization) and 300 Oe (after polymerization), would indicate that the annealed CoPt is crystallized in fcc structure.

ACKNOWLEDGMENTS

This work was supported by research Grants No. DAAD19-99-1-0001 from the Army Research Office and Grant No. (2001-04)-RII-03 from the LA Board of Regents, NSF/LEQSF.

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