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Co–Pt nanoparticles encapsulated in carbon cages prepared by sonoelectrodeposition

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Abstract

Co–Pt nanoparticles encapsulated in carbon cages have been prepared by sonoelectrodeposition followed by annealing in a CO atmosphere. Sonoelectrodeposition is a useful technique to make metallic nanoparticles, using ultrasound during electrodeposition to remove nanoparticles as they grow on the cathode surface. We used an electrolyte containing chloroplatinic acid and cobalt chloride and found that the atomic ratio of Co:Pt in the as-formed materials varied from 0.2 to 0.8 as the deposition current density was changed from 15 to 35 mA cm⁻². However, the as-deposited materials were inhomogeneous, comprising a mixture of Pt-rich and Co-rich nanoparticles. X-ray diffraction indicated that subsequent heat treatment (700 °C for 1 h) under CO gas created an ordered CoPt alloy phase that exhibited hard magnetic properties. Transmission electron microscopy showed many of the resulting nanoparticles to be encapsulated in carbon cages, which we ascribe to Co-catalyzed decomposition of CO during annealing. The thickness of the carbon cages was about ten layers, which may have helped reduce sintering during annealing. The size of the resultant nanoparticles was about 100 nm diameter, larger than the typical 5–10 nm diameter of as-deposited nanoparticles.

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

1. Introduction

Co–Pt particles have attracted much attention for their prospective use in magnetic applications, including ultrahigh-density magnetic storage media, due to the high magnetocrystalline anisotropy of the ordered L_{10} structure [1, 2], in which Co and Pt atoms occupy alternating (100) planes. The hard magnetic properties of this ordered face-centered tetragonal (fct) CoPt alloy are caused by the hybridization of the 3d and 5d electrons of Co and Pt, respectively. The alloy exhibits a saturation magnetization, $M_{\rm s}$, of 1.0 T, a Curie temperature, $T_{\rm c}$, of 840 K, and a crystalline anisotropy, K_1 , of 4.9 MJ m⁻¹ [3]. However, CoPt typically exists in either a disordered face-centered cubic (fcc) alloy phase, in which the statistical distribution of the Co and Pt atoms is substitutionally random, or in an only partially ordered fct alloy phase;

neither alloy achieves the same magnetic performance as the $L1_0$ alloy. The ordered phase can be obtained from the disordered phase (or vice versa) at elevated temperatures [4], but such annealing also tends to cause sintering, eliminating desirable geometric properties including size monodispersity. Beside the equiatomic composition of CoPt, the ordered alloys Co₃Pt and CoPt₃ are also known to be stable and adopt an $L1_2$ structure that has less favorable magnetic properties [5]. Ordered Co-Pt materials are normally obtained from disordered materials via an order-disorder transition, but sometimes have been obtained from pure Co and Pt layers via the diffusion of the two materials at high temperatures [6]. It is therefore preferable to isolate the magnetic material and prevent sintering by encapsulating the particles within a non-magnetic shell, such as graphitic carbon or silica [7, 8]. Creation of a core-shell structure can also be advantageous

by conferring other favorable physical or chemical properties, such as bio-compatibility [9, 10], suppression of inter-particle magnetic interactions or simply the prevention of unwanted oxidation [11]. In particular, confinement of nanoparticulates within multi-walled carbon nanotubes or in spherical graphitic cages has been demonstrated for a number of material systems and may lead to nanoscale hybrid systems with unique optical or electronic properties [12].

There are several ways to make Co-Pt nanostructured materials, including physical techniques such as arcmelting [13], thin film deposition (e.g. sputtering [14], low energy cluster beam deposition [15] or pulsed laser ablation [16]), chemical methods [17], and physicochemical methods such as electrodeposition [18], which is the technique employed here. Electrodeposition is a simple and inexpensive method for obtaining metallic materials [18]. The electrodeposition process can be divided into three Firstly, metallic particles are formed on the stages. surface of the cathode; secondly, the particles become dendrites [19]; and finally the dendrites develop to create metallic films. Co-Pt thin films have been widely prepared by electrodeposition using a flat cathode. Other Co-Pt morphologies such as nanowires have also been synthesized via deposition within nanoporous alumina membranes [20]. In contrast, the preparation of Co-Pt nanoparticles has been mostly via solution-phase chemical techniques. To our knowledge, Co-Pt nanoparticles have never been fabricated by sonoelectrodeposition (sonoel). Sonoel is a technique combining the advantages of electrodeposition and mechanical waves of ultrasound to produce metallic nanoparticles [21]. In this paper, we report on a method to obtain nanoparticles by electrodeposition and show that subsequent heat treatment can be used to encapsulate the Co-Pt nanoparticles within carbon cages.

2. Experimental details

A titanium horn of diameter 1.3 cm acted as both the cathode and ultrasound emitter (Sonics VCX 750). The electroactive part of the sonoelectrode was the planar circular surface at the bottom of the Ti horn while an isolating plastic jacket covered the immersed cylindrical part. This sonoelectrode produced a sonic pulse that immediately followed a current pulse. One pulse driver was used to control a galvanostat and the ultrasonic processor, which was adapted to work in pulsed mode. A home-made galvanostat (used without a reference electrode) was used to control the constant current regime. A platinum plate, 1 cm² square, was used as a counter electrode. The density of the current pulse was varied between 15 and 35 mA cm^{-2} at voltages between 4 and 5 V. The ultrasound power was 100 W. The duration, t_{on} , of the current pulse was 0.5-0.8 s then the current was turned off for a fixed duration, t_{off} , of 0.5 s. During t_{on} , Co-Pt nanoparticles were deposited on the surface of the electrode. Once the current was switched off, a 0.2 s ultrasonic pulse was used to dislodge the nanoparticles from the electrode. The volume of the electrolysis cell was 80 ml and contained 10 mM l⁻¹ H₂PtCl₆, 100 mM l^{-1} CoCl₂·6H₂O and 0.525 M l^{-1} Na₂SO₄, which

Table 1. Chemical composition of as-prepared Co–Pt nanoparticles and the magnetic properties of the annealed Co–Pt nanoparticles obtained from various current densities (*J*), coercivities (H_c , H'_c see text for definition), saturation magnetization (M_s), reduced remanence (M_r/M_s). The error bound on composition is $\pm 0.5\%$.

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J (mA cm ⁻²)	$H_{\rm c}^{\prime}$ (Oe)	H _c (Oe)	$M_{\rm s}$ (emu g ⁻¹)	$M_{\rm r}/M_{\rm s}$	Co (at.%)	Pt (at.%)
15 20 25 30 35	6900 6400 6000 4500 1100	11 500 9 500 11 000 11 700 1 100	35 38 40 41 62	0.73 0.66 0.48 0.42 0.40	45 47 51 60 80	55 53 49 40 20

were mixed under N2 atmosphere and held at room temperature throughout. A solution pH of 3 was controlled by addition of H₂SO₄. After deposition, Co-Pt nanoparticles were collected using a centrifuge (Hettich Universal 320, 9000 RPM, 20 min). Nanoparticles were dried in air at 80 °C for 20 min. All samples were then annealed at 700 °C for 1 h under a carbon monoxide (CO) atmosphere (≈ 1 bar) to reduce residual oxides. The crystallography of the nanoparticles was analyzed using a Bruker D5005 x-ray diffractometer (XRD). Magnetic measurements were conducted using a DMS-880 sample vibrating magnetometer (VSM) with a maximum magnetic field of 13.5 kOe at room temperature. The microstructure of the material was determined using an FEI Tecnai TF20 transmission electron microscope (TEM) that was equipped with a field emission gun (FEG) and operated at an acceleration voltage of 200 kV. The chemical composition of the Co-Pt nanoparticles was studied via energy dispersion x-ray spectroscopy (EDX) in TEM using an EDAX spectrometer and also by scanning electron microscopy (SEM) using a JEOL 5410 LV. The thermal behavior was examined by a differential scanning calorimetry (DSC) STD 2960 (TA Instruments) over the temperature range of 25-750 °C and with heating rates of $10 \,^{\circ}\text{C} \,\text{min}^{-1}$ under flowing argon.

3. Results and discussion

The concentration of Co and Pt deduced from the SEM–EDX results is shown in table 1. Beside the Co and Pt peaks, some O peaks are also qualitatively present. Using current densities of 15–25 mA cm⁻², the materials are close to the equiatomic composition that is of greatest interest although many are Co-rich in composition. At high current densities, the atomic percentage of Co was high because the standard electrode potential Co²⁺/Co (0.28 V) is less positive than that of Pt⁴⁺/Pt (0.742 V [22]) and so Co is expected to be deposited faster.

A low-magnification TEM image of typical as-prepared Co–Pt nanoparticles, synthesized using a current density of 20 mA cm⁻², is presented in figure 1(a). Other samples showed very similar features, exhibiting the same type of structural and compositional variations. The electron-transparent material predominantly comprises small, often geometrically regular nanoparticles/grains of a few nanometers in diameter (figures 1(b) and (c)). Occasionally, much thicker and larger nanoparticles are embedded within this



Figure 1. TEM and EDX analysis of typical, as-prepared Co–Pt nanoparticles, prepared using a current density of 20 mA cm⁻². (a) Large, self-supporting agglomeration of nanoparticulate and dendritic material. (b) Detail of a typical area, indicating clear compositional inhomogeneities. (c) HRTEM image of agglomerated nanoparticulate material. (d) EDX analysis of the two regions circled in (a), indicating the nanoparticulate material to be Co-rich and the darker material to be Pt-rich. There is almost complete phase separation of Pt and Co/CoO_x. Trace Fe contamination was detected in this, but not in later, samples and does not affect bulk measurements.

matrix. Note that the material in figure 1(a) straddles a hole in the carbon support substrate and therefore must be fused together rather than being a loose agglomeration of particles; such agglomeration is not unexpected since particles are not synthesized to have a co-ordination shell of ligands that would maintain particle separation. At low magnification (figure 1(a)), a slightly dendritic or wire-like morphology is apparent. EDX measurements within selected areas of the material are shown in figure 1(d). Area (1) is Co-rich, with a substantial O signal that is consistent with Co oxide formation, while area (2) is Pt-rich and contains little oxygen. In closeups of the material (figures 1(b) and (c)), the particles with size of about 5-10 nm are gathered into clusters. It is clear from the lattice fringes that all particles are crystalline. The fact that the as-deposited material has an inhomogeneous elemental distribution, consisting of Co-rich and Pt-rich particles rather than disordered fcc Co-Pt particles contrasts with many previous reports [23-25] in which composition analysis was not studied microscopically.

XRD patterns of the Co–Pt nanoparticles prepared with current densities of $15-35 \text{ mA cm}^{-2}$ are presented in figure 2(a). The patterns of all five samples are quite similar, with three strong peaks arising from (111), (200) and (220)

diffraction at scattering angles of 40.1°, 46.4° and 68.2°, respectively. From the (111) diffraction peak, we obtained the lattice parameter of 3.89 ± 0.01 Å for fcc structure of the asdeposited samples. This value is close to the lattice parameter of fcc platinum (3.92 Å) and far from the value of the fcc disordered CoPt (3.75 Å [23]). In previous reports [24–26], the authors ascribed those peaks to the diffraction of the fcc disordered phase. In fact, in this case we find that they arise from diffraction from near-pure Pt. The peaks of pure Pt are not so close to those of fcc Co-Pt but the broadening of the peaks due to the small size of the particles prepared by electrodeposition makes the diffraction peaks difficult to separate from the fcc Co-Pt peaks. Any diffraction peaks from Co are very weak due to the fact that their atomic weight is much less than that of Pt, a similar problem to that of the XRD analysis of FePt foils prepared by cold deformation [27]. The Pt peaks in the as-prepared samples are broad due to the small size of the particles. Using Scherrer's formula for the strongest peaks (111), a particle size of 7.5 nm has been obtained. The as-prepared particles were not disordered Co-Pt but they were formed by many Co-rich and Pt-rich small particles. There are also weak peaks around 36°, consistent with the presence of Co₃O₄ and suggesting that the Co-rich nanoparticles were oxidized, in agreement with the TEM-EDX.



Figure 2. (a) XRD patterns of the as-prepared Co–Pt nanoparticles with the current density of 15, 20, 25, 30, 35 mA cm⁻². (b) Comparison of XRD patterns of the as-prepared and annealed nanoparticles with the current density of 20 mA cm⁻². The o subscript index in Miller index denotes the ordered phase.



Figure 3. DSC trace for the as-prepared Co–Pt nanoparticles (heating rate $10 \,^{\circ}$ C min⁻¹) shows a broad peak at about $350 \,^{\circ}$ C.

We conclude that separate populations of Pt-rich and Co-rich particles have been synthesized and that the direct formation of fcc Co-Pt by electrodeposition did not occur. A heterogeneous product is not unexpected and is similar to the heterogeneous CoCu thin films that are typically prepared by electrochemistry [28]. The process may be explained by the difference in the standard electrode potentials of Co^{2+}/Co and Pt^{4+}/Pt . In essence, reduction of Pt^{4+} to Pt requires a relatively large voltage while a smaller voltage is required to reduce Co^{2+} , leading to differences in deposition rate. In terms of the product structure, nanoparticles form through the reduction and attachment of metallic ions at the cathode surface. If the deposition continues, two sequential processes can occur: (1) the development of nanoparticles followed by (2) the fusion of nanoparticles into dendrites and, ultimately, into continuous thin films [19]. In sonoel, the sonic waves act as mechanical agitation that limits the fusion of nanoparticles, yielding a product that has characteristics midway between isolated nanoparticles and dendrites, as illustrated by the images of figure 1, where both the particulate nanostructure and the

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slightly more dendritic appearance at longer lengthscales are apparent.

Turning now to the post-synthesis annealing process, the thermal behavior of as-synthesized Co-Pt samples further supports the observation of a heterogeneous composition. Figure 3 presents the DSC trace for Co-Pt nanoparticles in the temperature range of 25–750 °C, collected under a heating rate of $10 \,^{\circ}\text{C} \,\text{min}^{-1}$. There is a broad peak centered around 350 °C. It is known that the order-disorder fcc-fct transition in continuous media is characterized by a relatively sharp peak in the range of 367–440 °C with a full width at half maximum of 56–120 °C at the heating rate used here [29]. The much broader peak in the DSC response in the present case is not surprising given the heterogeneous nature of the sample. Alloying of separate populations of Co-rich and Pt-rich nanoparticles will be a kinetically limited process that is slowed by the need for substantial sintering, mass-transfer and diffusion and should therefore give rise to a much broader feature in DSC. Nevertheless, both fundamental and ordered diffraction peaks of the ordered phase are presented in figure 2(b). There is a small peak next to the (111) main peak of the ordered Co-Pt which can be assigned to a Pt-rich phase—CoPt₃. The presence of this phase implies the incomplete diffusion between Co- and Pt-rich nanoparticles, which we attribute below to the presence of carbon layers around the nanoparticles.

Figure 4 presents TEM bright-field and the dark-field images of some typical regions of an annealed sample that was prepared using a current density of 30 mA cm⁻² and subsequently annealed in the presence of CO at 700 °C for 1 h. Much of the material is too dense to image effectively, as substantial sintering and agglomeration has occurred, but the looser material at the edge of large clusters is sufficiently thin for TEM analysis. The bright-field images indicate the result of sintering. The size of the particles has increased significantly after annealing, from diameters of a few nanometers for the as-prepared particles to a few tens of nanometers afterward. Dark-field imaging is a particularly useful way of viewing the sample. A number of low-order diffraction rings have been selected to form an image, then superimposed as a false-color RGB image to highlight the spatial distribution



Figure 4. TEM and EDX analysis of typical, annealed Co–Pt material, prepared with a current density of 30 mA cm⁻². (a) Bright-field TEM image of a typical cluster of material. (b) Red–green–blue superposition of three dark-field images, using distinct electron diffraction rings to pick out different material types. Most of the dark nanoparticulate matter in (a) appears encapsulated in a lighter material, here colored red. (c) Another typical area with (d) EDX collected from the two indicated areas. EDX analysis of area 1 yields only a strong carbon signal whilst the EDX results from area 2 indicate the presence of Co and only trace Pt. ((e), (f)) HRTEM images of typical encapsulated nanoparticles, with (inset) the central portions of their respective Fourier transforms to indicate the good crystallinity of both core (sharp spots/streaks in the Fourier transform) and the well-defined ring that arises from the carbon shell.

of material types. The choice of color shading is arbitrary but areas of the same color contribute to the same diffraction ring and are therefore typically composed of the same crystalline material. The composite dark-field TEM images clearly indicate structural and compositional inhomogeneity and a distinctive core–shell appearance for many of the nanoparticles. High resolution TEM (HRTEM) images of the material (figures 4(e)and (f)) allow the core and shell components to be resolved. Both structures are crystalline, with typical cubic ordering in the core but circumferential lattice fringes in the shell. TEM–EDX (figure 4(d)) indicates that the shell material is carbon while the core material is predominantly Co. Indeed, negligible Pt was detected from the nanoparticle in area 2, suggesting that the Pt resides predominantly in the thicker, agglomerated material. Thus, the sample comprises Co-rich particles encapsulated in carbon-

onion cages, typically with a few tens of graphitic carbon layers surrounding each particle. Similar particles have been observed elsewhere [30]. Most particles have a rounded profile, characteristic of annealing and some show evidence of twinning—the existence of more than one crystallographic domain.

Before annealing, EDX indicated that carbon was not present in the material. Upon heat treatment under a carbon monoxide atmosphere, Co–Pt nanoparticles encapsulated in carbon cages were formed. Thus, the formation of the observed carbon-onion shells must be related to the heat treatment process. It has previously been reported that carbon monoxide decomposes readily into carbon and carbon dioxide in the presence of metallic catalysts [31] and can lead to the formation of carbon nanotubes. In the presence of catalytic nanoparticles such as Co, Fe or Ni, carbon monoxide has a simple decomposition reaction, making it an ideal carbon precursor for carbon nanotubes synthesis at elevated temperatures:

$$2CO (gas) \leftrightarrow CO_2 (gas) + C (solid).$$

Kinetic and thermodynamic factors limit the effective CO decomposition reaction to a temperature range of 520-800 °C at normal pressure [32]. The presence of Pt nanoparticles however supports the conversion of CO to CO2 therefore the formation of carbon after annealing can be ascribed to Co nanoparticles [33]. In our annealing conditions (700 °C, 1 atm. pressure), the mole fraction of CO/CO_2 is about 0.6/0.4. Increasing the CO pressure shifts the effective CO decomposition reaction temperature to higher temperatures. There is also a known association between the precipitation rate and the obtained products. A higher flow rate, and consequently faster cooling and carbon precipitation rates, favors the formation of carbon nanotubes, while a slower precipitation rate yields encapsulated metal particles [32]. The flow rate when annealing Co-Pt nanoparticles was slow, two bubbles per minute, which therefore facilitated the formation of encapsulating graphitic layers. In addition, according to the Ellingham diagram [34], the formation enthalpy of CO₂ by oxidation of carbon is constant and indifferent of the temperature, while the formation enthalpy of CO is a decreasing line. The Boudouard reaction [35] implies that at lower temperatures the equilibrium is on the exothermic carbon dioxide and at higher temperatures the endothermic formation of carbon monoxide is the dominant product. At 700 °C, which is the annealing temperature of our sample, those two trends are comparable, therefore with the presence of Co as a catalyst, the formation of CO₂ and C is preferable.

The significant change observed in the size of the particles before and after annealing is consistent with sintering and will be enhanced by the known depression of the melting point of metallic nanoparticles with respect to the bulk [36]. Using the expression for the melting temperature in [37], at a particle size of 5-10 nm, the melting point of Co particles is calculated to be 600–700 °C, much lower than the melting point of bulk Co, 1495 °C [38]. Thus, even at a temperature of 700 °C, substantial sintering is expected, with large particles growing



Figure 5. Magnetization curves of the as-prepared Co–Pt nanoparticles with the current densities of 15–35 mA cm⁻².

at the expense of smaller particles. The DSC curve (figure 3) did not show an endothermic peak in that region but a fast reduction in the DSC signal, which may be explained by a large size distribution of the material before annealing. The size of particles in the annealed samples was limited to about 100 nm, probably because the carbon shells prevented aggregation to form larger particles.

Magnetization curves of the as-prepared samples are presented in figure 5. All curves indicate magnetic hysteresis with a coercivity, H_c , of ≈ 300 Oe and a saturation magnetization, M_s , from 2 to 5 emu g⁻¹. The values of $M_{\rm s}$ in the as-prepared samples are much smaller than those reported previously and may again indicate partial oxidation or hydroxidation of Co to form antiferromagnetic cobalt oxides, as suggested above by EDX and XRD. After annealing, the magnetization curve indicates the formation of the hard magnetic Co-Pt phase. Figure 6 presents the hysteresis loops of the annealed sample prepared with a current density, J, of 15 mA cm^{-2} . The curves for $J = 20, 25, 30 \text{ and } 35 \text{ mA cm}^{-2}$ are similar to that of 15 mA cm^{-2} . Typical hard magnetic behavior is indicated from the hysteresis loops with large coercivities. It is important to note that, because of the limit in maximum applied field of 13.5 kOe, the hysteresis loops are minor loops. Therefore, the real coercivities must be larger than the values obtained here. When $J = 15 \text{ mA cm}^{-2}$. the sample had high M_s and H_c . When J was changed from 15 to 30 mA cm⁻², samples showed hard magnetic properties with a kink at a low reversed magnetic field of 300 Oe, which indicates that there was a small amount of a soft magnetic phase. Classically, the coercivity is defined as the field for which the magnetization (M) vanishes (H'_c) . In a more physically meaningful definition, the coercivity $H_{\rm c}$ may be defined as the field where the largest number of moments reverses, i.e. the maximum of the susceptibility (dM/dH). In most cases, both definitions of the coercivity are almost equivalent. However in multiphase materials, these two definitions differ significantly [39]. From figure 6(b) and



Figure 6. (a) Hysteresis loop of the annealed Co–Pt nanoparticles with the current density of 15 mA cm⁻² and (b) some magnetic parameters of annealed Co–Pt nanoparticles as a function of the current density. Annealing conditions: 700 °C, 1 h.

table 1, H'_c was 7 kOe whereas H_c was 11 kOe. Coercivity achieves a maximum value (equal or higher than 11 kOe) in the samples with the chemical composition of the particles close to the equiatomic composition, i.e. samples with J of 15–30 mA cm⁻². Specifically, when the current density, J, is reduced, the coercivity increases and for J = 15 mA cm⁻², when an equiatomic composition is obtained, H_c is greater than or equal to 11 kOe. Increasing the current density causes an increase Co content, resulting in the high M_s . However, the magnetic squareness M_r/M_s reduced with J because of the presence of the Co₃Pt (see figure 6(b)). Some magnetic parameters of the annealed samples are given in table 1.

4. Conclusion

Co–Pt nanoparticles encapsulated in carbon cages have been prepared by sonoel. A core–shell structure was obtained by annealing the nanoparticles in a CO atmosphere, with HRTEM and EDX characterization indicating metallic cores and a carbon-onion shell. Carbon-onion formation was explained through catalytic decomposition of carbon monoxide and may be of benefit in preventing nanoparticle sintering. Hard magnetic properties of the nanoparticles were indicative of the formation of an ordered Co–Pt phase.

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