

STRUCTURAL TRANSFORMATION STUDY OF CoPt PARTICLES FOR HIGH DENSITY RECORDING MEDIA

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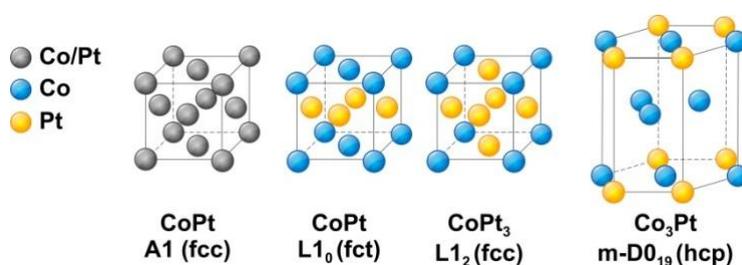
Received 11 April 2017; accepted 06 May 2017

1. Introduction

High density magnetic storage technologies require materials with smaller grain size but with high coercive fields to overcome superparamagnetic limit [1]. Recent progress is founded on nanomaterials on the base of FePt and CoPt alloys, which show great ability to achieve extremely small grain size and high value of coercive field. It turns out that the FePt and CoPt nanoparticles with $L1_0$ (fct) structure have great potential to serve as future ultrahigh-density data storage media [2].

The structure of the $L1_0$ ordered phase is based on a face centered cubic (fcc) lattice with alternating Fe (or Co) and Pt planes stacked along one of the $\langle 011 \rangle$ direction [3, 4]. Scheme 1 shows structure variability of CoPt alloy. A1 phase is stable for equiatomic CoPt above 825°C, below which $L1_0$ phase is formed. The A1 phase is chemically disordered where Co and Pt atoms randomly occupying the positions in fcc lattice. $L1_2$ structure is formed at 75% platinum content by quenching process. Co atoms occupy the corners of fcc lattice, whereas Pt atoms occupy the face-centered positions. Co_3Pt hcp phase does not occur in bulk phase diagram. Metastable Co_3Pt was reported in the thin films [5, 6]. These facts advert to consequence of an annealing treatment at transformation from A1 phase into $L1_0$ (fct) phase, which presents hard magnetic properties. Sun et al. [7] studied thermal annealing of FePt core-shell nanoparticles. The value of coercive field varied from 0 kOe to 6 kOe depending on annealing temperature (450 – 600°C).

In this paper, we report study of structural transformation core-shell CoO@Pt nanoparticles prepared by reverse micelle method [8]. We have focused on structure transformation in these nanoparticles with the aim to understand the processes, which can affect future application of CoPt solid solutions as data storage media. Structural changes were observed by transmission electron microscopy, X-ray in-situ measurements and by magnetic measurements.



Scheme 1 Structure variability of CoPt alloy.

2. Experimental

The CoO@Pt nanoparticles were synthesized by the reverse micelle technique using $CoCl_2$ and H_2PtCl_6 as metal precursors, aqueous solution of borohydride ($NaBH_4$) as

reducing agent, cetyltrimethylammonium bromide (CTAB) as surfactant, butanol as co-surfactant, octane as oil phase and water as dispersion phase. Briefly, CTAB solution in octane and butanol, aqueous CoCl_2 was added to form reverse micelle solution. Sodium borohydride (NaBH_4) was then added to the micelle solution to reduce the metal precursor to a metallic state. An additional micelle solution was added to the reaction mixture containing aqueous H_2PtCl_6 to form a passivating shell. The Pt precursor was reduced by additional NaBH_4 solution. The reaction mixture was allowed to age for 1 h before being washed with methanol:chloroform (1:1) solution to remove surfactants. Prepared nanoparticles were dried at 80°C in the air.

In situ X-ray measurements were realised at beamline P02.1, PETRA III (DESY, Hamburg) by X-ray radiation with energy 60 keV at detector distance 413.22 mm. Experiment was carried out by setup containing thermally regulated furnace (hot blower) and sample static holder. Sample was gradually heated from 22°C up to 720°C , subsequently annealed at 720°C during 3 hours and repeatedly cooled down to 30°C . Sample was placed into Quartz Glass capillary with outside diameter 0.8 mm. As calibrant was used cerium dioxide CeO_2 .

Prepared and annealed nanoparticles (NPs) were investigated by transmission electron microscope JEOL 2100 operating at 200 kV. Sample powder was dispersed by ultrasonication in methanol and was spilled on carbon coated grids.

Magnetic properties were investigated using a MPMS-XL5 (Quantum Design) apparatus in the external dc field up to 5 T and in the temperature range of 2-300 K.

3. Results and discussion

The crystal structure of the CoO@Pt nanoparticles was determined by X-ray in-situ measurements. Fig. 1 a) shows XRD spectra of as-made particles. Peak positions correspond to CoPtO_2 (ICSD #31916), Pt (ICSD #64923) and CoO (ICSD #29082) phases. Cobalt oxides are presented in as-made particles because of surface oxidation. This indicates that the as-prepared nanoparticles are composed of Co core with surface oxidation and Pt shell. Low intensity values of CoPtO_2 phase show that this component is present in a small amount. X-ray in-situ measurements (Fig. 2 a)) were used to study casting process of core and shell into one alloy. We have investigated structural changes by examination of lattice parameter calculated from detected reflexions (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) for symmetry group $F 4/m -3 2/m$ using pseudo-Voigt function:

$$V(x) = \alpha \frac{1}{\pi w} \frac{1}{1 + \left(\frac{x - x_0}{w}\right)^2} + (1 - \alpha) \sqrt{\frac{\ln(2)}{\pi}} \frac{1}{w} \exp \left[-\ln(2) \left(\frac{x - x_0}{w}\right)^2 \right]$$

where w is the half-width at half-maximum ($2w = \text{FWHM}$), x_0 is the position of the Bragg peak and α the Lorentzian content. The mixing factor α may have any value in the interval $\langle 0, 1 \rangle$. The mean size of coherently scattering domains estimated from as-prepared NPs X-ray pattern by Williamson-Hall function was $D_{\text{XRD}} = 24.11$ nm with lattice parameter 0.3903 nm and density 21.8 g/cm^3 . Fig. 2 b) shows development of lattice parameter during whole annealing process (red) and change of temperature (blue). Lattice parameter linear increases up to 200°C and then with additional heating on the 700°C decreases from 0.3911 nm to 0.3835 nm. We assume this change of lattice parameter is caused by Co atoms diffusion into Pt lattice, what resulting into structure densification. Other heat treatment at 700°C during 3 hours had no effect on the lattice parameter and it remained constant. X-ray pattern of studied sample was compared with peak position of CoPt (A1, ICSD # 102621), CoPt ($L1_0$, ICSD #102620) and CoPt_3 ($L1_2$, ICSD #102624) phases. Measured peak positions and intensities

are in good agreement with $L1_2$ phase, but it cannot be exclude the presence of $L1_0$ phase in the sample. The annealed nanoparticles had lattice parameter 0.3835 nm, the domain mean size $D_{XRD} = 110.51$ nm and density 109.49 g/cm³ (estimated from X-ray data).

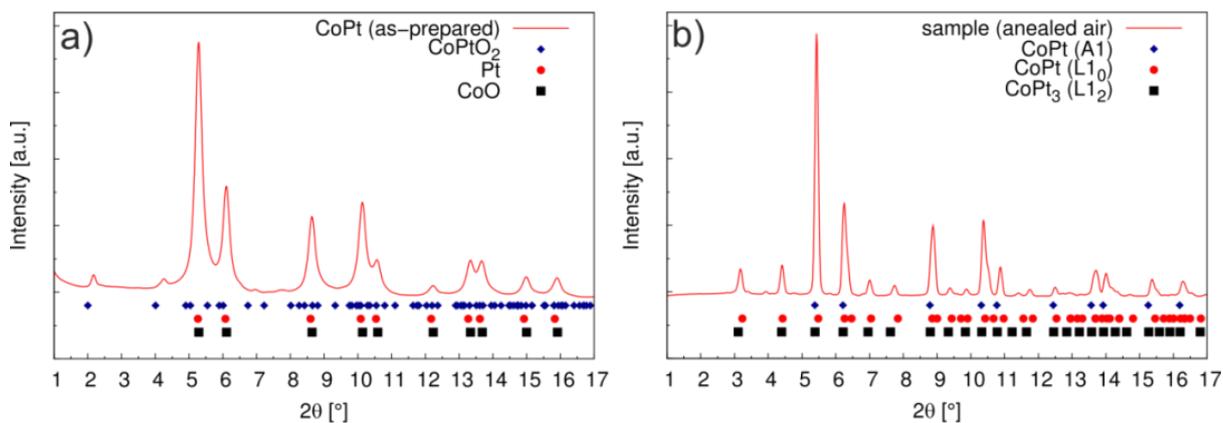


Fig. 1 X-ray patterns a) before annealing, b) after annealing.

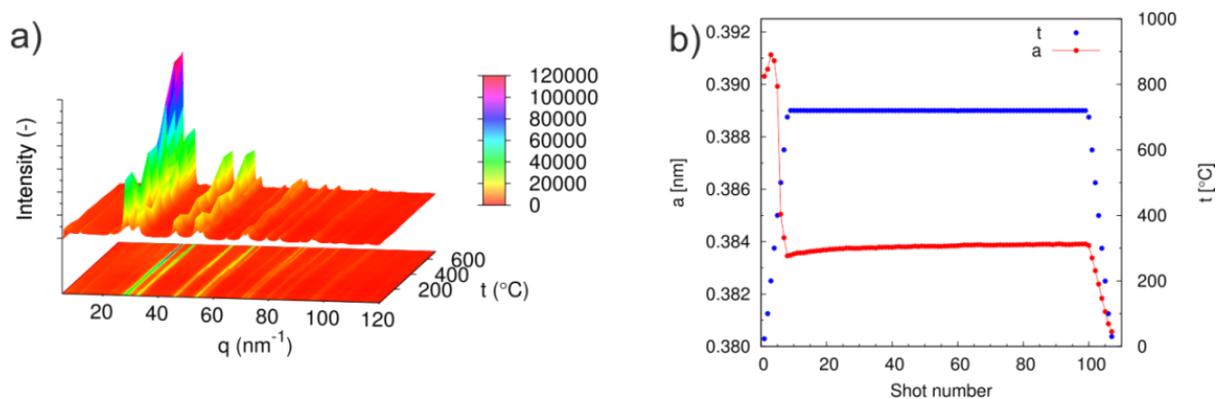


Fig. 2 a) In-situ X-ray measurement patterns, b) lattice parameter and temperature changes during annealing process.

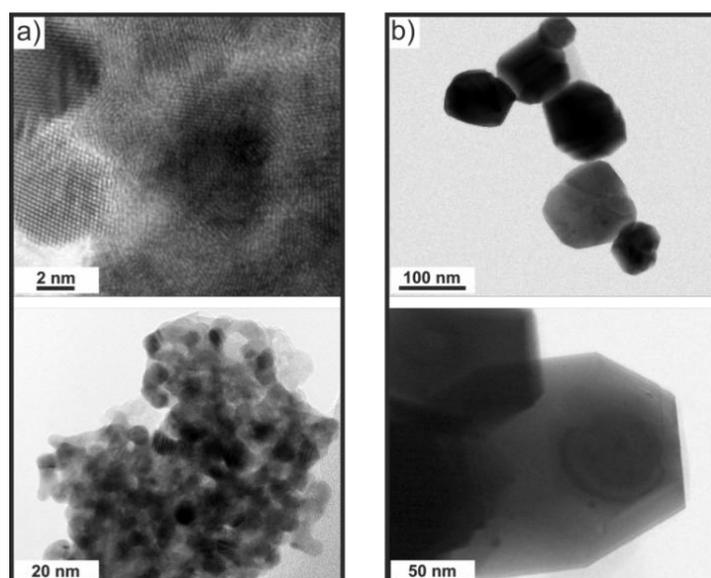


Fig. 3 TEM images of a) as-prepared and b) in air annealed CoO@Pt NPs.

TEM images for as-prepared as well as for annealed nanoparticles in the air are shown in Fig. 3. A log-normal distribution analysis yields nanoparticle diameter of $D_{\text{TEM}} \sim 4.0$ nm. It is seen from Fig. 3b, that after thermal treatment the size of nanoparticles increased on the diameter $D_{\text{TEM}} \sim 110$ nm. A large difference between D_{XRD} and D_{TEM} values of as-prepared NPs shows a greater relevance of TEM measurement for the determination of particle size, whereas X-ray measurements contains information about the mean size of coherently scattering domains which may or may not be equal to the particle size.

As-prepared CoO@Pt NPs display a superparamagnetic behaviour at room temperature, see Fig. 4a (red curve). Magnetic moment obtained by the fit of Langevin function fit equal to value of $223 \mu_{\text{B}}$. At a temperature of 2 K (blue curve), the NPs exhibit coercivity $H_{\text{C}} = 10^3$ Oe and a saturation $M_{\text{S}} = 29.81$ emu/g. After thermal treatment by annealing at 720°C in the air, Fig.4b, the value of saturation magnetization M_{S} significantly decreases ($M_{\text{S}} = 2.88$ emu/g) and $M(H)$ curve at 2 K (blue curve) exhibits a low coercivity $H_{\text{C}} = 150$ Oe. Change in magnetic behaviour after thermal treatment is caused by interdiffusion of Co atoms into Pt lattice. This observation confirms formation of soft magnetic particles with $\text{CoPt}_3 \text{L1}_2$ structure.

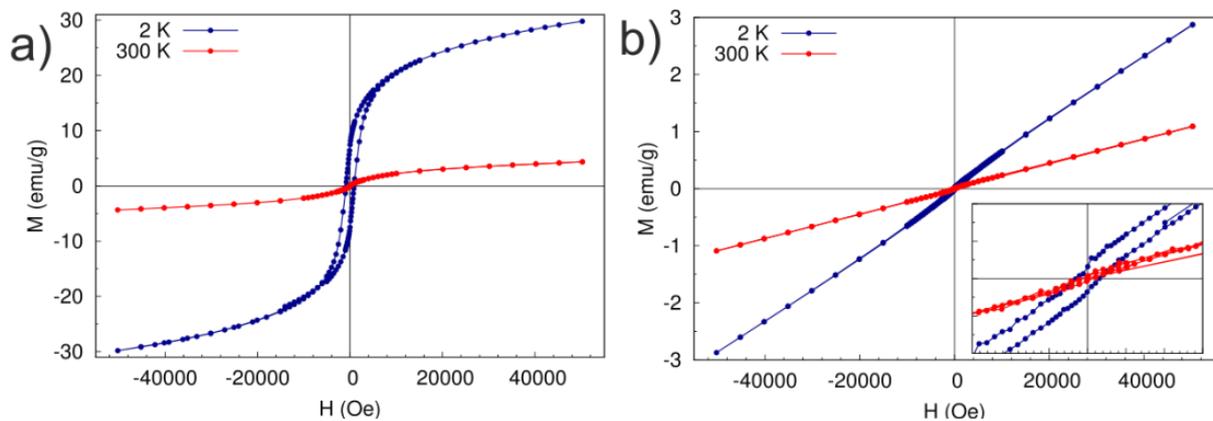


Fig. 4 Magnetization curves at 2 K and 300 K for a) as-prepared nanoparticles, b) annealed nanoparticles (inset shows detail of curves).

4. Conclusion

We have studied structural transformation of CoO@Pt core-shell nanoparticles annealed in the air by X-ray in-situ measurements, TEM and by magnetic measurements. As-prepared nanoparticles display a superparamagnetic behaviour caused by fine CoO core. During annealing process at 720°C , the size of nanoparticles enlarged from $D_{\text{TEM}} \sim 4$ nm to $D_{\text{TEM}} \sim 110$ nm. After annealing superparamagnetic properties were suppressed by formation of a magnetically soft $\text{CoPt}_3 \text{L1}_2$ phase.

Acknowledgement

This work was supported by the Slovak Research and Development Agency under the contracts APVV-15-0115 and APVV-15-0520, by the VEGA No. 1/0377/16, No. 1/0745/17 and faculty of science grant VVGS-PF-2016-72646. Authors would like to thank V. Girman for realization of TEM measurements.

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