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TEM *in situ* experiment as a guideline for the synthesis of as-grown ordered CoPt nanoparticles

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Abstract. Co_xPt_{1-x} nanoparticles on amorphous alumina are synthesized by a finely tuned Pulsed Laser Deposition (PDL) technique. By means of an alternate deposition experiment using pure Co and Pt targets, we have shown that the composition of the nanoparticles can be controlled with a precision of 2%. This composition varies linearly with the lattice parameter of the nanoparticles following the well known Vegard law. During the synthesis, the substrate temperature is a key parameter to control the structure and the morphology of the nanoparticles. We have performed an *in situ* heating experiment in an electron microscope using disordered Co₅₅Pt₄₅ nanoparticles to study their thermodynamic behavior. We have observed both ordering within the nanoparticles and coalescence between the nanoparticles. The temperature regimes evidenced by the *in situ* experiment are used to determine the temperature of the substrate to synthesize as-grown L1₀ ordered nanoparticles with a better control on their size and composition.

1. Introduction

The control of nanoparticle size and structural arrangement are essential challenges in nanofabrication. These parameters are particularly important in the case of CoPt and FePt bi-metallic nanoparticles since they govern their magnetic properties. These alloys exhibit, in the bulk state, a phase transition between a tetragonal chemically ordered phase (L1₀) at low temperature and a disordered Face Centred Cubic (FCC) structure at high temperature. The L1₀ ordered phase, due to the alternative atomic stacking of pure Co or Fe and pure Pt layers, has large magnetocrystalline anisotropy. By means of this magnetic property, important research efforts are devoted to study L1₀ ordered nanoparticles which are expected to be the future information storage media for extremely high density recording (EHDR) [1, 2].

Among the different physical techniques currently used, only few succeed in obtaining as-grown L1₀ structure for FePt and CoPt alloyed nanoparticles [3]. The disordered structure (A1 phase) is largely predominant for a growth temperature ranging from 20°C to 600°C. This is a non-equilibrium structure compared to the bulk state phase diagram (figure 1) [4, 5]. The ordered structure is obtained

usually by a post-synthesis annealing at temperature higher than 600°C. Because of this elevated annealing temperature ($\sim T_m/2$, T_m being the melting temperature of the bulk alloy), this procedure may induce coarsening or coalescence of the nanoparticles, which results in a particle size out of the range considered for EHDR [2, 6]. Indeed, considering an area density of nearly 1Tbit/in² for the next generation of hard disks, the bit dimension will reach a nanometric size of approximately 10 nm [7]. Avoiding the annealing step would be a clear technological breakthrough, and numerous research groups aim at the fabrication of ordered as-prepared nanoparticles by optimization of growth parameters. In the case of vapour phase deposition techniques, adjustments of key parameters like the deposition rates, the nature of the substrate [8] and particularly the temperature of the substrate can improve dramatically the ordering of the as-grown nanoparticles, without having recourse to annealing.

In this paper we show how a finely tuned pulsed laser deposition (PLD) experiment on amorphous alumina results in ordered as-grown CoPt nanoparticles. In a first part, we show that we can reliably select any composition for the Co_xPt_{1-x} nanoparticles. Then, to better understand the role of the substrate temperature on the degree of order and on the morphology of CoPt nanoparticles embedded in alumina, we performed *in situ* heating experiments in a transmission electron microscope (*in situ* TEM). The temperature regimes observed during the *in situ* experiments are used to optimize the PLD parameters. Finally, the growth mechanisms during the synthesis and the key role of temperature in the ordering and coalescence mechanisms are discussed.

2. Experimental procedures

2.1 Sample preparation

The CoPt nanostructured thin films on amorphous alumina (a-Al₂O₃) were produced by pulsed laser deposition in a high vacuum chamber. The pressure in the chamber is better than 10⁻⁷ mbar. A typical target-substrate configuration is used to deposit separately the a-Al₂O₃ and the metals by PLD using a KrF excimer laser at 248 nm with pulse duration of 25 ns at repetition rates in the range of 1 to 20 Hz. The laser energy can be chosen in the range of 150 to 250 mJ depending on the ablation threshold of the selected target. The distance from targets to substrate was approximately 5 cm. Samples are obtained by alternated irradiation of the two metal targets to produce the plasma of each metal. The substrates used were commercial TEM grids on which we have deposited an amorphous carbon layer with a thickness of 10 nm. On the top of the amorphous carbon, a 3 nm layer of a-Al₂O₃ was deposited using our PLD setup. Then, cobalt and platinum were alternatively deposited using pure Co and Pt targets. The deposition rate of each element is controlled by an *in situ* quartz crystal monitor, which indicates the thickness of deposited materials on the quartz surface. This thickness is then defined as the nominal thickness in a continuous film approximation. The deposition rate depends on the target nature and on the laser frequency. In this work, all the samples were synthesized with a laser

frequency of 5 Hz. With this frequency, the ablation rates are respectively 3 nm, 0.15 nm and 0.02 nm per minute for $\alpha\text{-Al}_2\text{O}_3$, cobalt and platinum. The quantity of Pt and Co deposited at each step depends on the targeted composition. In addition, to insure a good homogeneity of the film, the nominal thickness corresponding to two successive steps (one Co and one Pt) is set to 0.1 nm. During the deposition, the substrate is held at a fixed temperature T_s , between room temperature and 725°C. At the end of synthesis, samples were covered by a 3 nm thick layer of $\alpha\text{-Al}_2\text{O}_3$ in order to protect alloys from air oxidation. The various tuneable experimental parameters in PLD technique allow a high control on vapour-phase growth with slow deposition rate.

2.2 *In situ* heating experiment

In situ TEM is a powerful method to observe order-disorder phenomena in metallic alloys. *In situ* annealing has been performed using the GATAN heating specimen holder model 652 which allows heating from room temperature to 1000°C. The thermal stability of the sample during the heating procedure is promoted by very efficient water cooling. The evolution of the sample morphology was followed in bright field mode and the structural transformation in diffraction mode performed on a JEOL 4000FX electron microscope operating at 400kV. The experimental protocol has been defined by taking into account the equilibrium regions of the phase diagram of the bulk CoPt material (figure 1). It was however slightly modified during the experiments as a function of the evolution of the observed phenomena. The heating procedure used to observe the ordering-disordering process on a selected area was as follows: the temperature was progressively increased from 25°C up to 600°C (in 50 minutes). Then, the temperature was increased by steps of 30°C every 10 minutes, until 700°C. Then, the steps have been reduced to 15°C every 20 minutes, from 700°C to 850°C. After half an hour at 850°C we started the temperature decrease by steps of 30°C every 10 minutes until 570°C and finally, the sample was cooled down to room temperature in one hour.

First of all, heating procedure was performed on $\text{Co}_{45}\text{Pt}_{55}$ bulk sample in order to check the temperature calibration of the heating holder. For this composition the CoPt phase diagram exhibits a narrow two phase stability region at 780°C (figure 1). During the experiment, this first order phase transition has been observed at 815°C indicating that the temperature given by the thermocouple of the heating holder may differ from that of the sample by a few tens of degrees. In addition, when using carbon film deposited on copper grids, the temperature is not perfectly homogeneous on the carbon film and slightly changes with the distance from the copper bar. Therefore, during the *in situ* experiments, we have always observed the same area of the sample.

3. Results

3.1 Control of the nanoparticles composition

The synthesis of nanoparticle films by the PLD method has been previously realized with a single target containing the Co and Pt elements at chosen concentration [9]. However, because cobalt and platinum have widely differing vapour pressures, the stoichiometry of the ablated target is not reproduced in the collected nanoparticle film. Instead of using a single target, we show here that the alternate use of two pure metal targets allows a composition-controlled synthesis of homogeneous nanoparticle films. Moreover, this approach has the obvious advantage that we can easily select any composition. We have first synthesized seven samples to cover the whole composition range between pure Co and pure Pt. The nominal thickness of the samples was 2.5 nm and the substrate temperature was fixed at 550°C. The as-grown nanoparticles are not chemically ordered and their size is in a range from 10 to 20 nm. Energy Dispersive X-Ray spectroscopy (EDX) was performed on large areas (0.4 μm) of the samples. The lattice parameter of the FCC structure was determined by means of electron diffraction measurements calibrated with reference of the bulk $\text{Co}_{45}\text{Pt}_{55}$ alloy. Because the substrate is amorphous, the nanoparticles are randomly oriented on the surface and the diffraction diagram displays a typical ring pattern characteristic of a powder-like diffraction. We found that the composition of the films is homogeneous on each TEM grid within the accuracy of EDX measurements (2% at.) and we showed that it varies linearly with the lattice parameter of the nanoparticles (figure 2). In addition, the values presented in figure 2 are close to the line joining the values of the bulk Co to that of the bulk Pt [10], *i.e.* close to the Végard law observed for the electrodeposited CoPt thin film [11]. A behaviour close to that of the thin film is consistent with the rather large size of the nanoparticles (above 10 nm in diameter) for which the size effect on the lattice parameter is small [12].

Note that we can now use the curve presented in figure 2 to deduce the composition of the disordered nanoparticle films using the lattice parameters obtained by electron diffraction. More importantly, following the experimental protocol improved during the course of the above study, we are now able to synthesize homogeneous $\text{Co}_x\text{Pt}_{1-x}$ nanoparticle films of any composition, with a measured composition closer than 2% to the targeted value.

3.2 Order-disorder and coalescence phenomena

To study the phase transition from chemically disordered FCC phase to the L1_0 chemically ordered phase, the *in situ* heating protocol described in the experimental procedures section (part 2.2) was performed on CoPt nanoparticles assemblies obtained for a nominal thickness of 2 nm (figure 3a). This sample, with a $\text{Co}_{55}\text{Pt}_{45}$ composition, was prepared with a substrate temperature of 500°C and has been covered by a 3 nm thick $\alpha\text{-Al}_2\text{O}_3$ layer. As-grown nanoparticles observed at room temperature have a coverage on the substrate close to 67% and the nanoparticle size range from 5 nm to 25 nm.

The coverage was determined by measuring, using TEM bright field images, the percentage of the Al_2O_3 substrate covered by the nanoparticles. At this temperature, the tendency of the metal to wet the surface results in nanoparticles of irregular shapes elongated in the plane of the substrate, which makes it difficult to define their mean size from a statistical point of view (figure 3a). The mean distance between the particles is close to 4 nm. As shown by the diffraction pattern in the inset of figure 3a, the particles are in the disordered FCC phase.

Increasing the temperature up to 600°C in 50 minutes had no significant influence on the nanoparticles mean size, but the nanoparticle morphologies tend to be slightly more spherical (figure 3b). However, the superstructure 001 ring appears at 570°C and it is clearly visible on the electron diffraction of figure 3b at 600°C. Therefore, at temperatures above 570°C, atomic diffusion inside the nanoparticles is fast enough to drive the transformation to the ordered L1_0 structure. We can also note that this 001 ring has a diffuse intensity, which can be either due to short range ordering or due to the nucleation of small ordered domains on the surface or in the volume of the nanoparticles. During the next steps of the heating, the intensity of superstructure reflections increases rapidly and the diffuse ring is replaced by a sharp one. It is also expected that the $\text{FCC} \rightarrow \text{L1}_0$ phase transition changes the values of the lattice parameters. By comparing the interplanar spacing calculated from the position of the 001 and 110 superstructure rings, we observe that the initial cubic structure becomes tetragonal. The c/a ratio of the tetragonal structure decreases to 0.97 (*i.e.* $a = 3.782 \text{ \AA}$ and $c = 3.669 \text{ \AA}$), which is very close to the value in bulk alloys [13].

No visible evolution of the morphology takes place during the heating procedure from 600°C to 690°C at the rate of 30°C every 10 minutes. When reaching 710°C, the particles start to coalesce, resulting in larger and thicker particles. The size increase of the nanoparticles is also visible on the electron diffraction pattern where sharp diffraction spots appear along the diffraction rings. The sample morphologies observed after 20 minutes at 740°C (figure 3c) show a broadening of the size distribution of the particles from 5 nm to 80 nm. After 20 minutes at 750°C (figure 3d) the size distribution of the particles is bimodal. The first population has a mean particle size of 5 nm whereas the second one has a mean particle size in the range of 20 to 100 nm. Note also that the small particles have an almost spherical shape and that the larger ones have a platelet-like shape. This point has been established at the end of the *in situ* experiment by tilting the sample in order to get different projected images of the particles.

Detailed inspections of figures 3c and 3d and also video recording bring some clues about the coalescence mechanisms. Two coalescence mechanisms are distinguished in the literature: (a) static coalescence when the nanoparticles are immobile and coalesce by mutual rearrangement of their surface and (b) dynamic coalescence when the nanoparticles are mobile and coalesce together upon contact [14, 15]. The latter phenomenon was not observed during our experiments. This can be due to different reasons: it occurs too rapidly to be detected or it concerns too small particles or it is inhibited by the presence of the Al_2O_3 film. The first phenomenon takes place by atomic rearrangement of two

close enough nanoparticles, leading to the formation of atom inter-diffusion bridges [16]. These bridges are well visible on the examples arrowed in figures 3c and 3d. This mechanism can be favoured by the growth of the nanoparticles supplied by the diffusion of Co and Pt atoms in the Al_2O_3 matrix, through the well known Ostwald ripening phenomenon [17]. This mechanism involves the growth of large particles at the expense of smaller ones, when the substrate is annealed at high temperature. This coalescence results in a drastic evolution of the coverage down to 52% and an increase of the mean inter-particles distance up to 8 nm (figure 3d). At 750°C the system reaches a morphological stability: the morphology of the film does not evolve anymore during the heating up to 850°C in 130 minutes, and also during half an hour step at 850°C as well as during the temperature decrease to room temperature in 150 minutes. This stability is due to the fact that both inter-particles distance and particle size become very large which inhibit their static and dynamic coalescences.

During the coalescence phenomenon, we observe at 750°C the disordering of the nanoparticles (see electron diffraction in the left inset of figure 3d). This temperature is close to the order-disorder transition temperature (785°C) expected from the bulk CoPt phase diagram for this alloy composition (figure 1), taking into account the temperature difference between the heating system and the sample (a few tens of degrees) and the accuracy of the composition measurements ($\pm 2\%$). This is consistent with the fact that, in this range of size (a few tens of nanometers), nanoparticles have the same thermodynamic behaviour than the bulk material. The temperature, at which the disordering appears, is expected to be lower for the smallest nanoparticles. However, a dedicated *in situ* experiment, using a smaller density of nanoparticles to avoid the coalescence mechanisms and a lower heating ramp would be necessary to reveal the phenomenon.

After heating up to 850°C, we have decreased the temperature to test the reversibility of the transition. At 715°C, few sharp diffraction spots appear on the position of the 001 ring, and at 700°C the superstructure rings are clearly visible (see electron diffraction in the right inset of figure 3d). The appearance of the first sharp diffraction spots is probably due to the ordering of the largest domains. Note that the temperature at which order is observed, 715°C, differs from the temperature at which the nanoparticles become disordered during the heating ramp (750°C). This difference may be partly explained by the delay between the temperature heating / cooling of the sample and of the sample holder or by a kinetic effect. However, at these temperatures, the atomic diffusion is much faster than the temperature ramp (30°C every 10 min). We have checked that this phenomenon is not observed for the bulk sample. It is therefore likely that this hysteresis can be either due to a surface effect influenced by the alumina matrix [18] or due to the low thermal conductivity of the alumina insulating layer [8]. EDX analysis shows that the composition of the particles remains unchanged during the *in situ* experiment. Further work is underway to clarify this point.

4. Discussion

To summarize the *in situ* TEM experiment, we have characterized the morphological and structural evolution of an initially disordered Co-Pt nanoparticle film. The initially disordered particles order at 570°C and coalesce at 710°C inducing a rapid increase of the particle size. We now comment on the temperature dependence of the order phenomena and of the coalescence processes observed in our experiment. First, the ordering of the initially disordered nanoparticles is a kinetic process, requiring atomic jumps both at the surface and in the bulk of the nanoparticles. So, the temperature at which order is observed is not a quantity of thermodynamical equilibrium, and depends on the annealing time. However, because diffusion is a thermally activated process, the diffusion coefficients evolve very strongly with temperature. Therefore, when increasing temperature, the transition between a process ‘too slow to be observed in a reasonable time’ and a rapid process is usually very fast. That value of the temperature of transition between these two regimes can be estimated by assuming that the mean diffusion length (γ) equals to the first nearest neighbour distance [19]. The mean diffusion length is given by:

$$\gamma = \sqrt{Dt} = \sqrt{D_0 \exp\left(-\frac{E_a}{kT}\right)t}$$

where D is the diffusion coefficient, t the time, D_0 the pre-exponential factor, E_a the activation energy, k the Boltzmann constant and T the temperature in Kelvin. We have chosen the impurity diffusion of Pt (in Co) since, owing to its size it is the least diffusing constituent of the alloys. Using the values $D_0 = 0.65 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ and $E_a = 279.3 \text{ kJ mol}^{-1}$ [20], and $t = 10$ minutes as the characteristic annealing time in our experiment, the transition is found close to 550°C. This estimation is in a good agreement with our experiment where an annealing temperature above 570°C is necessary to really observe ordering of the particles. This conclusion is also consistent with the observation of the disordered structure for as-grown Co-Pt nanoparticles when the substrate temperature is well below 600°C [21, 22]. Similarly, the temperature at which the coalescence is observed has a kinetic origin. In addition, we want to stress that this temperature may also slightly differ between in a sample with a very high coverage of particles (as the one used in the *in situ* experiment) and in a sample containing well-isolated nanoparticles.

Our objective was to use the results of the *in situ* experiment to optimize the choice of the substrate temperature during the PLD synthesis. Before doing so, it is important to stress the limits of this approach. First of all, during a PLD synthesis, the nanoparticles are formed in a highly out-of-equilibrium condition, which differs from a simple annealing of the nanoparticles. Secondly, the nanoparticles observed *in situ* are covered with alumina, and this is obviously not the case during the PLD synthesis. We therefore expect that the temperature at which the coalescence is activated inside

the PLD apparatus is smaller than the one suggested by the *in situ* experiment. The temperature range that can be used to obtain small as-grown ordered nanoparticles is thus smaller than the (570°C-710°C) range.

We have selected a substrate temperature of 650°C, roughly in the middle of the temperature range suggested by the *in situ* experiment. The other parameters of the PLD synthesis are unchanged (laser frequency of 5 Hz and nominal thickness 2 nm). After the synthesis, the as-grown nanoparticles are characterized using TEM. When compared to the sample obtained at 500°C, the particles have a more regular shape, often close to a sphere. EDX analysis, in a nanoprobe mode, has shown that they also have a $\text{Co}_{55}\text{Pt}_{45}$ composition. Moreover, the coverage (51%) is lower than the one observed at 500°C indicating that the growth is more three-dimensional. The size distribution of the particles (right inset of figure 4a) is close to a Gaussian with a mean size of 7.6 nm and a standard deviation of 3.3 nm. Most importantly, the as-grown nanoparticles are ordered in the L1_0 structure as it is shown on the electron diffraction pattern of the nanoparticles (left inset of figure 4a). The same synthesis protocol has been realized with a substrate temperature of 725°C. In this case, the histogram of the particle sizes (right inset of figure 4b) indicates a bimodal size distribution with a first size population from 1.5 to 3.5 nm and a second one centred on 10 nm. Moreover the coverage has been reduced to 42%. The largest particles are polycrystalline suggesting that the first particles formed during the synthesis have coalesced. In this scheme, new nucleation sites become available on the substrate between the coalesced nanoparticles [23] making possible the growth of smaller CoPt nanoparticles in the late stage of the synthesis. The electron diffraction (left inset of figure 4b) shows the ordered state of these nanoparticles. Moreover, on both samples, the order is also clearly visible on HREM images of the nanoparticles. Figures 4c and 4d show nanoparticles of 5 nm oriented along the [001] direction and 8 nm oriented along the [112] direction, coming from the samples respectively heated at 650°C and 725°C during the synthesis. The power spectrum of each image clearly shows the superstructure reflections (encircled in insets of figures 4c & 4d) characteristic of the tetragonal L1_0 structure oriented along the [001] and [112] directions.

5. Conclusion

We have synthesized as-grown L1_0 ordered CoPt nanoparticles using a PLD experiment where the substrate temperature was selected on the basis of an *in situ* annealing experiment in a transmission electron microscope. Moreover, the size of the particles has been shown to depend on the temperature of the substrate. Thus, controlling the temperature and the amount of matter deposited on it makes possible the manufacturing of as-grown L1_0 ordered nanoparticles of definite size, density and composition. Even if the particles size distribution is still not narrow enough to be used in the magnetic applications for EHDR, the control of the structural and morphological parameters are very promising from the point of view of magnetism studies and applications. It becomes therefore possible to directly synthesize film of nanoparticles chemically ordered and magnetically isolated. Additional

work is currently under progress to quantify the degree of order as a function of the particles size, and to study their magnetic properties.

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Figures and figure captions:

Figure 1. Equilibrium phase diagram of bulk CoPt.

Figure 2. Rectangles: Atomic percent of Cobalt measured by EDX and FCC lattice parameter, determined on electron diffraction patterns, in $\text{Co}_x\text{Pt}_{1-x}$ nanoparticles samples. **Line:** Végard Law deduced from the values of the FCC lattice parameter of pure bulk Co and Pt metals.

Figure 3. Evolution of a selected area as a function of increasing temperature observed in bright field and electron diffraction modes (diffraction pattern in the inset) **(a)** 25°C, the diffraction pattern has been indexed according to the FCC structure; **(b)** 600°C; **(c)** 740°C, the diffraction pattern has been indexed according to the $L1_0$ structure; **(d)** Morphology of the area at 750°C which has remained unchanged during the temperature decrease down to 700°C. *Left inset:* 750°C during the temperature increase, after the order-disorder phase transition. *Right inset:* 700°C during the temperature decrease, after the disorder-order phase transition. The **arrows** show atom inter-diffusion bridges between nanoparticles.

Figure 4. CoPt nanoparticles grown at $T_s = 650^\circ\text{C}$ (a & c), $T_s = 725^\circ\text{C}$ (b & d). Electron microscopy images in Bright Field mode, corresponding diffraction patterns (left inset) of as-grown ordered CoPt nanoparticles and size distributions of the particles in the right inset (a & b). HRTEM images and power spectra of ordered nanoparticles, (c) projected along the $[001]$ direction, (d) projected along the $[112]$ direction. The ordered reflections of the $L1_0$ structure are encircled. Images acquired on a JEOL 2010F electron microscope.