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STEM Nanodiffraction Technique for Structural Analysis of CoPt Nanoparticles

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Abstract

Studying the structure of nanoparticles as a function of their size requires a correlation between the image and the diffraction pattern of single nanoparticles. Usually, nanobeam diffraction technique is used but TEM investigations are long and tedious, particularly on nanoparticles randomly oriented on an amorphous substrate. We bring a new development to this structural study by controlling the nanoprobe of the Bright and Dark Field STEM (BF/ DF STEM) modes of the TEM. The particularity of our experiment is to make the STEM probe parallel using a fine control of the focal lengths of the microscope illumination lenses. This technique coupled to the drift correction feature of digital STEM allowed to obtain diffraction patterns of several single nanoparticles selected on the STEM image. By means of this technique, we highlighted size effects on the order – disorder phenomena in CoPt nanoparticles with a size smaller than 3 nm.

Introduction

In nanoscience, the knowledge of the atomic arrangement of nanoparticles is of fundamental importance because their physical and chemical properties are usually very sensitive to this arrangement [3-5]. It is well known that, in nanoparticles where the proportion of surface atoms is large, the equilibrium structures may differ from the one predicted by the equilibrium phase diagram of the bulk material. Therefore, nanoparticles can exhibit, as a function of their size, structural transformation due to the competition between surface and volume energies [1, 2].

In order to study the structural properties of nanoparticles, it is necessary to be able to synthesize nanoparticles assemblies with a well controlled size which is generally a difficult experimental task. Indeed, synthesis of nanoparticles by physical routes on amorphous substrate leads to randomly oriented clusters with a broad size distribution, generally between 10 to 30 % of the mean particles size. If we are interested in characterizing the structure of nanoparticles, as a function of their size, it is then necessary to use techniques that combine both image and diffraction information at the nanometer scale. In addition, to obtain statistical results it is important to perform this structural analysis on a large number of particles.

The most widely used techniques are the high resolution transmission electron microscopy (HRTEM) and the nanobeam diffraction (NBD) by using an almost parallel beam of nanometric size combined with conventional Bright Field or Dark Field (BF/DF) imaging. These methods however can not give statistical information because of the following limitations:

(i) On HRTEM images we directly observe the morphology and the structure of the particles, but each analysis requires zone axis orientation conditions. Moreover, due to the small lattice parameters, particularly in the case of metallic nanoparticles, the current point to point resolution of electron microscope only permits to observe the structure of particles oriented along the low indexes zone axes. Due to this strong reduction of the analysis possibilities and to the necessity to analyze many particles, the determination of the nanoparticles structures is a very tedious task using HRTEM, particularly when nanoparticles are randomly oriented.

(ii) The NBD technique gives diffraction patterns of single nanoparticles but is not limited by small lattice parameters of the metallic particles. Any diffraction patterns of single nanoparticles contain useful information. However, as for the HRTEM technique, nanoparticles have to be oriented along a zone axis in order to determine their structure without any ambiguity. In addition, NBD has the drawback to give an indirect correlation between the morphology and the structure. This correlation requires the acquisition of an image of each analyzed particle and to switch from image to diffraction mode. This step is sometimes difficult on an assembly of almost identical nanoparticles.

The difficult step of the orientation of each nanoparticle may be overcome by developing epitaxial growth of nanoparticles on suitable crystalline substrates. However, the structure of the nanoparticles can strongly be influenced by the epitaxial relationship and the induced stress between the particles and the substrate.

In this paper, we present a new method based on the use of the STEM mode imaging in a TEM with illumination conditions very close to the ones used in nanobeam diffraction experiments. We will show, how the use of this technique has allowed us to emphasize a size effect on the equilibrium structure of the CoPt nanoparticles prepared by Pulsed Laser Deposition (PLD).

STEM nanodiffraction technique using parallel illumination conditions

The experiments have been performed on a JEM-2100F (TEM/STEM) field emission electron microscope operating at 200 kV. The microscope is equipped with a high resolution objective lens pole piece ($C_s = 0.5$ mm, point-to-point resolution at the Scherzer defocus = 0.19 nm in TEM mode). Nano-beam diffraction patterns were obtained in the STEM mode condition, which was performed by using the digital STEM system of the microscope. The illumination system of new generation TEM is constituted by a four stage lens system. In such optical systems, the electron beam is focused on the specimen by two condenser lenses C1 and C2, a condenser mini-lens (CM) and a Pre-Field Objective lens (PFO). The probe size and the convergence angle 2α of the beam are determined by the currents in this set of lenses and the size of the condenser aperture. In conventional TEM imaging conditions, (BF, DF and HRTEM) the illumination has to be almost parallel. This is done by modifying the focal lengths in C1, C2 and CM to adjust the position of the cross-over point (COP) at the position of the pre-focal plane of the PFO (Figure 1a). Generally, the condenser aperture size is 100 µm.
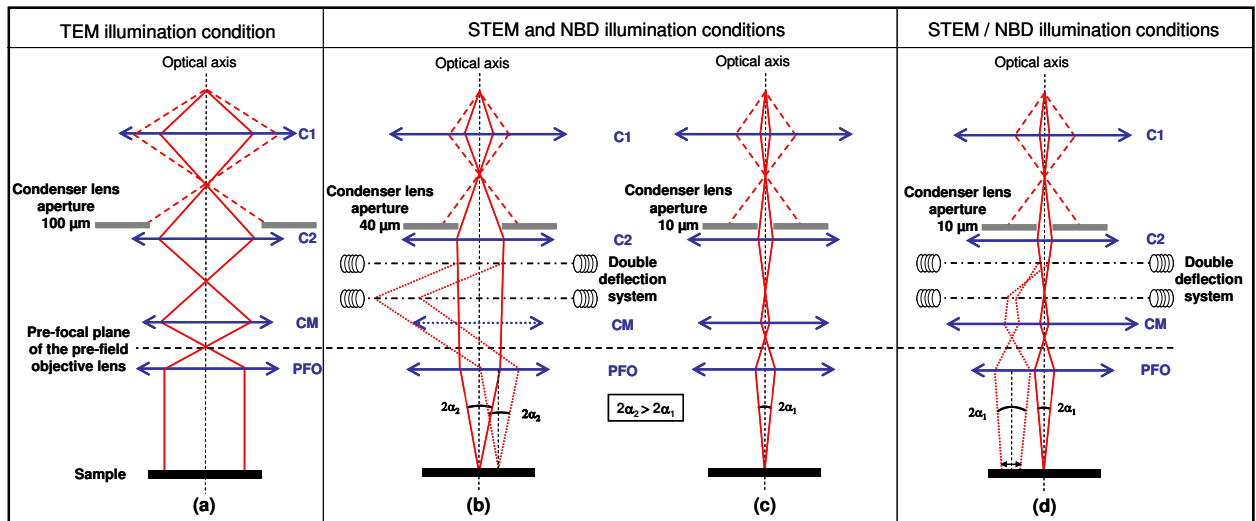

Figure 1: Ray diagrams of the illumination system (C1 and C2: Condenser lenses; CM: Condenser Mini lens; PFO: Pre-Field Objective lens). (a) Parallel beam condition in conventional TEM – (b) Conventional STEM condition – (c) Conventional NBD condition – (d) STEM / NBD condition (large dashed lines: stopped beam by the condenser aperture; dotted lines: deflected beams by the scanning system)

In STEM illumination condition (figure 1b), the CM lens is off, and the focal lengths of C1 and C2 are fixed to form a beam almost parallel with a propagation direction along the optical axis. We used a 40 μm diameter condenser aperture. The quasi-parallelism of the beam between the C2 and the PFO lenses has two consequences. Firstly, it avoids the distortion of the beam during the scanning process performed by a double deflection system. It preserves the size of the probe whatever the position of the beam in the plane of the sample. Secondly, this almost parallel beam is focused on the sample (size probe of 0.7 nm) by the PFO inducing a large convergent angle characteristic of the STEM mode. Nanodiffraction in convergent beam condition was developed by Cowley using a dedicated STEM microscope to measure medium range order on amorphous material and to determine the helicity of single wall carbon nanotubes [6, 7]. This illumination condition was not used in our experiments due to the very large convergence angle of the beam. This large angle induces large diameter of the diffracted spots leading to a lack of precision in the determination of d_{hkl} distances. Moreover due to the coherence of electron beam, interference effects take place between overlapping diffraction spot. The intensities of the reflections in the area of the overlap are strongly affected by the relative phase of the reflections making difficult quantitative intensity measurements.

To carry out our experiment, the microscope is first aligned in the NBD mode. The focal lengths in C1, C2 and CM are fixed to form the COP slightly ahead of the pre-focal plane of the PFO (Figure 1c). In these conditions, using the smallest available condenser aperture (10 μm), the convergence angle 2α of the electron beam was less than 1 mrad and the beam diameter on the specimen was 1 nm. All the currents of the lenses are saved. The TEM is then switched into the STEM mode but the lenses currents setting of the NBD mode are used for the illumination system (Figure 1d). The astigmatism of the probe has to be corrected by condenser stigmators using the Ronchigram. In addition, using such optical conditions, the scanning system between C2 and CM operates on a beam which is not parallel. It induces weak incorrigible image distortions due to the increase of the beam size when the probe moves away from the optical axis (as indicated by the double arrow in figure 1d). However, the images quality is good enough to combine STEM imaging functionalities with a 1 nm size quasi-parallel beam on the sample. The probe scanning system (*i.e.* image and spot modes) can be used to study, in diffraction mode, the structure of single nanoparticles.

The STEM images were recorded and memorized in the computer. The images were acquired in bright field mode by a BF detector. Positions of a lot of nanoparticles of different sizes were then marked on the computer display. The position of electron beam was controlled by the computer and the nano-beam diffraction patterns were projected on the image plane. Those patterns were recorded by CCD-camera (Gatan Erlangshen, model ES500W) automatically. During the diffraction patterns acquisition, the specimen drift was corrected by the drift-correction system in the STEM using cross-correlation function.

Recently, similar method has been developed by He and Nelson [8] on a Zeiss Libra 200 FEG microscope with Koehler illumination system. The particular illumination of this microscope allows to form a parallel beam of 80 nm in diameter to perform NBD in STEM mode. Even if it remains possible to acquire nanodiffraction on single nanoparticles, this can be done only on samples where the nanoparticles density is very low which is generally difficult to obtain using physical route synthesis. Moreover, due to the large beam diameter, the only way to acquire images with a good resolution is to use standard STEM conditions. The main problem is then to reduce the beam shift when switching between the parallel to the convergent configurations in order to probe the same area of interest in both diffraction and image modes.

CoPt nanoparticles preparation

The CoPt nanoparticles thin films on amorphous carbon were produced by pulsed laser deposition in an ultra high vacuum chamber. The pressure in the chamber is better than 10^{-7} mbar. A typical target-substrate configuration is used to deposit separately metals by PLD using a KrF excimer laser at 248 nm with pulse duration of 25 ns at repetition rate of 5 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 fixed at 5 cm. The substrates used were commercial TEM grids on which we have deposited an amorphous carbon layer with a thickness of 10 nm. Then, cobalt and platinum were alternatively deposited using pure Co and Pt targets. The number of pulses on the Co and Pt targets at each step was fixed in order to obtain the $Co_{50}Pt_{50}$ composition. The deposition rate of each element is controlled

by an *in situ* quartz crystal monitor, which indicates the nominal thickness of deposited materials on the quartz surface, in a continuous thin film approximation. As the metallic species do not wet carbon amorphous substrate, nanoparticles are formed instead of a continuous thin films and the nominal thickness of a sample obviously do not corresponds to the particle thickness. At a frequency of 5 Hz, the deposition rates are respectively 0.15 nm and 0.02 nm per minute for cobalt and platinum. Two samples with 1 nm and 2 nm in nominal thickness, have been prepared at a substrate temperature of 25°C. At the end of the synthesis, samples were covered by a 3 nm thick layer of a-Al$_2$O$_3$ deposited by PLD in order to protect alloys from air oxidation. Finally, the thin films have been annealed in a vacuum furnace during 1 hour at 700°C.

Results on CoPt nanoparticles

The equiatomic bulk CoPt alloy presents a phase transition at 825°C between a tetragonal ordered phase (L1$_0$) at low temperature and a disordered face centered cubic structure (FCC) at high temperature [9]. The L1$_0$ ordered phase has a large magnetocrystalline anisotropy which is at the origin of important research efforts devoted to study L1$_0$ ordered CoPt nanoparticles. Small bimetallic magnetic clusters are expected to be the future information storage media for extremely high density recording (EHDR) [10, 11].

Post synthesis CoPt nanoparticles are FCC disordered which is a non equilibrium phase compared to the bulk material phase diagram. This unexpected structure appears using vapour phase deposition techniques with a low substrate temperature, because the growth kinetics of the particles is faster than the ordering kinetics. The ordering mechanisms require a post-synthesis annealing over 600°C [12]. After a thermal annealing of 1 hour at 700°C, the particles obtained with a 1 nm nominal thickness have a mean size of 3 nm whereas the ones obtained with 2 nm nominal thickness have a mean size of 5 nm. On both samples, the polydispersity (standard deviation divided by the mean size of the nanoparticles) is around 33%. Order / disorder phenomena in these CoPt nanoparticles have been studied as a function of the particles size. The detection of order by using conventional selected area diffraction is inappropriate to our study due to the polydispersity. In consequence, the structure of the nanoparticles can only be studied on single nanoparticles, but we have to describe crystallographic data of the L1$_0$ structure before to present the results.

The L1$_0$ tetragonal structure (space group P4/mmm, a = 0.378 nm, c = 0.366 nm) is formed by alternative atomic stacking of pure Co and Pt layers along the [002] direction (figure 2). The atomic positions in the tetragonal lattice are: (0,0,0) and (½, ½, 0) for Co atoms and (½, 0, ½) and (0, ½, ½) for Pt atoms.
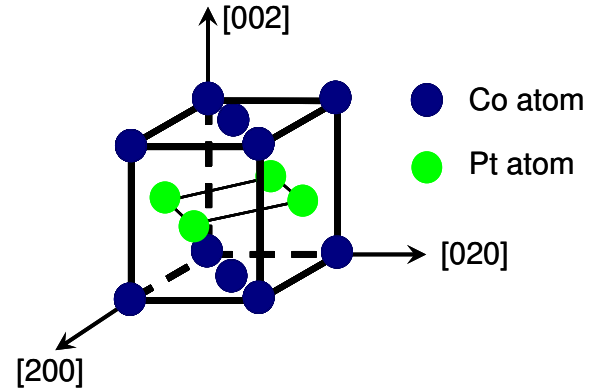

Figure 2: L1$_0$ ordered structure

According to this structure, we can define two types of diffracted reflections (the diffraction diagram being centrosymmetric each reflection g is associated to –g) : (i) the Fundamental Reflections (FR) type for which h, k and l are all odd or all even i.e. 111 ($\bar{1}\,\bar{1}\,1$ …), 002, 220 ($2\bar{2}0$ …) *etc* and (ii) the Superstructure Reflections (SR) type for which l can be even or odd and h and k have the same parity but different from the one of l *i.e.* 001, 110 ($\bar{1}10$ …), 112 ($\bar{1}12$ …) *etc*. The extinction rule is obtained when h and k have different parities. Due to this rule, when a particle is oriented along a [220] zone axis type, the [022] and [202] zone axes present only the FR whereas the [220] zone axis shows the 001 SR and the 110 type SR. In consequence, we cannot conclude on the order/disorder state of particle showing a diffraction pattern characteristic of the disordered phase oriented along the [220] zone axis type.

Only few zone axis orientations can evidence the L1$_0$ structure without any ambiguity. The [111] zone axis which has the three $\bar{2}20$ type reflections always presents the 110 SR if the nanoparticle is in the ordered phase. In the same way, the [002] zone axis presents the $\bar{1}10$ SR type and the [200] (or [020]) zone axis presents the 001 SR.

This strong limitation in the characterization of the order implies to perform statistical analyses of the nanoparticles in order to determine the morphological parameter influencing their structure. As it was pointed out in the introduction, HRTEM and NDB experiments are not suitable techniques for statistical analyses and we carried out the STEM NBD experiment described in the experimental part of this paper to considerably decrease the time of investigation.

Figures 3A and 3B show STEM BF images of the CoPt nanoparticles obtained respectively with 2

and 1 nm nominal thickness annealed during 1h at 700°C. The NBD diffraction patterns corresponding to the encircled particles in the STEM images are presented in figures 3 A1 to A4 and B1 to B4 respectively for both samples. The nanoparticles were chosen as a function of their dark contrast in order to obtain good diffraction conditions. The size, orientation and structure of the analyzed nanoparticles for both samples are summarized in table 1. By comparison with conventional BF TEM image we can estimate a precision of the measurements on the STEM / NBD image of ± 0.25 nm.
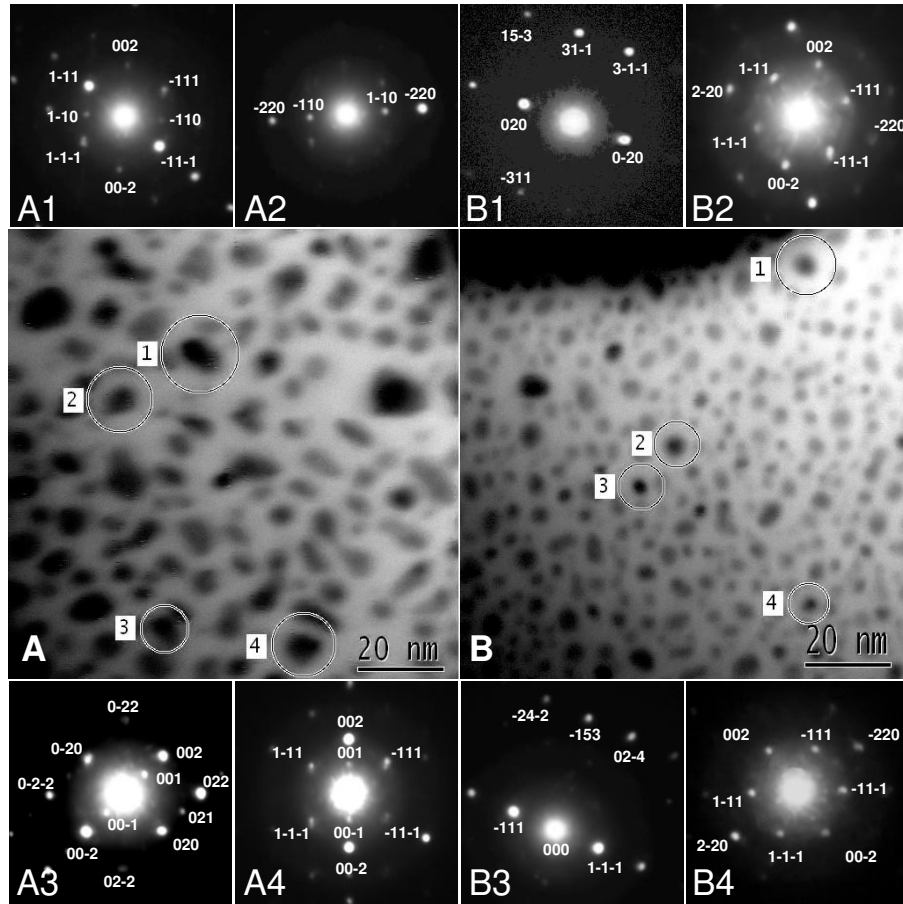

Figure 3 : STEM BF images of the CoPt nanoparticles obtained respectively with : (A) 2 and (B) 1 nm nominal thickness. NDB diffraction patterns A1 to A4 and B1 to B4 corresponding to the encircled particles in the STEM images (A) and (B) respectively.

	CoPt 2 nm (Fig 3A) Size and Orientation	Structure	CoPt 1 nm (Fig. 3B) Size and Orientation	Structure
Particle 1	5.7 nm : [220] zone axis	$L1_0$ ordered	3.3 nm : [103] zone axis	FCC disordered
Particle 2	5.0 nm : [220] systematic row	$L1_0$ ordered	3.4 nm : [220] zone axis	FCC disordered
Particle 3	4.5 nm : [200] zone axis	$L1_0$ ordered	2.3 nm : [321] zone axis	FCC disordered
Particle 4	6.0 nm : [220] zone axis	$L1_0$ ordered	2.0 nm : [220] zone axis	FCC disordered

Table 1 : Nanoparticles size and orientation of CoPt nanoparticles analyzed on the BF STEM images in figures 3A and 3B.

On the sample with 2 nm nominal thickness, we found superstructures reflections on only 44% of the acquired diffraction patterns on particles bigger than 3.5 nm (total number of analyzed particles: 230). However the result can be explain by the extinction rules. For example, we have considered the nanoparticles oriented along the [220] type zone axis. On this sample, we have observed 35 particles in this type of orientation. Among them, 24 do not present SR and 10 have the 001 and 110 SR. We find the 2/3 and 1/3 proportions expected from the crystallography rules for nanoparticles randomly oriented. These TEM investigations do not permit to determine the structure of each particle, but these statistical data are consistent with the fact that all the particles in this range of size are in the $L1_0$ ordered structure. In the case of the CoPt nanoparticles obtained with

1 nm nominal thickness, the SR are never present on the diffraction diagram of the particles whatever their orientation (total number of analyzed particles: 160).

These results clearly indicate the existence of a critical size under which the order–disorder phase transition temperature of CoPt nanoparticles decreases and is lower than 700°C. This critical size has been determined in the range from 3 to 3.5 nm. This range is in very good agreement with theoretical predictions made by Chepulskii *et al.* [13].

Due to the broad size distribution, nanoparticles smaller and larger than the size limit, determined in the previous experiment, can be found on the same sample with 2 nm nominal thickness. Figure 4A shows a STEM BF image where the nanoparticle labeled B has a size of 3 nm and the nanoparticle C has a mean size of 7.5 nm. The smaller is disordered, as it can be seen on the [111] zone axis diffraction of the particles presented in figure 4B whereas the bigger is in the $L1_0$ structure as it can be seen in the [111] zone axis shown in figure 4C. Since the [111] zone axis permits to evidence the $L1_0$ structure without any ambiguity, this result confirms the critical size which has been determined above.
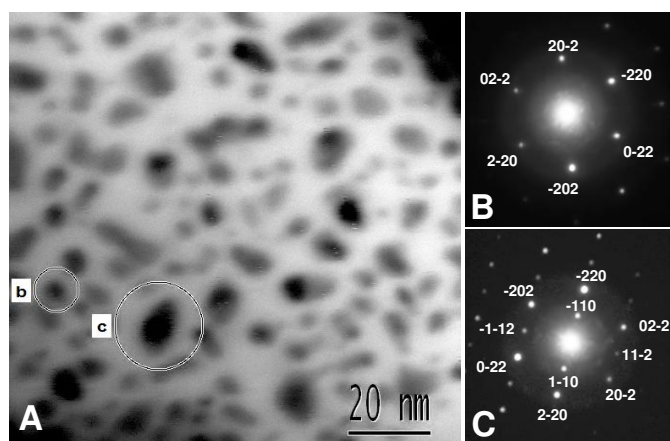

Figure 4: STEM BF image of CoPt obtained with 2 nm nominal thickness – (B) [111] zone axis of the particle b showing the disordered structure – (C) [111] zone axis of the particle c showing the $L1_0$ ordered structure.

Conclusion

TEM illumination conditions have been modified to develop parallel nanobeam diffraction experiment in STEM mode. By using the facilities of digital STEM nowadays available on new generation TEM, it is possible to control the beam and to analyze the structure of nanoparticles by diffraction and to obtain their image at the same time without changing the lenses configuration of the microscope. This technique has been applied to the structural study of CoPt nanoparticles and has demonstrated size effect on order disorder phenomena. This effect corresponds to a decrease of the phase transition temperature for particles with sizes smaller than 3 nm.

Finally, this technique will be used to acquire zero loss energy filtered diffraction patterns in order to measure quantitatively the diffracted intensity of superstructure and fundamental reflections. Further works are under progress to determine the order parameter on individual particles by comparing these measurements to dynamical theory calculations.

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