



	Experiment title: Coalescence versus size-dependant ordering transition of Co_xPt_{1-x} nanoparticles	Experiment number: SI-1809
Beamline: ID03	Date of experiment: from: 29 oct 2008 to: 04 nov 2008	Date of report: 18/07/09
Shifts: 18	Local contact(s): Dr. Andrea RESTA, Dr Roberto FELICI	<i>Received at ESRF:</i>
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Aim and experimental method:

With respect to bulk materials, surface-supported nanoparticles (NPs) offer additional degrees of freedom to tune the magnetic properties by controlled modifications of particle size and shape. These characteristics make Co or Fe nanosized systems attractive for fundamental studies as well as for miniaturized data-storage applications. The key role property is the magnetic anisotropy energy, which describes the tendency of the magnetization to align along specific directions rather than randomly fluctuate over time. The CoPt system maximizes the magnetic anisotropy energy of the Co 3d ferromagnetic phase, owing the strong spin-orbit coupling of Pt 5d states, especially in the tetragonal L1₀ CoPt phase. In order to achieve high uniaxial magnetocrystalline anisotropy induced by this structure, thermal annealing, during or after the NPs growth, is often required because the as-deposited particles at room temperature are in a chemically disordered structure. Such thermal assistance induces morphological changes (from non crystalline to crystalline morphologies) and chemical rearrangements (from disordered to ordered structures) in the NPs¹. Moreover, in the case of supported NPs, it may also modify the NPs size and dispersion on the substrate by coalescence or Ostwald-ripening mechanisms which can promote or inhibit the structural rearrangement.

For the effect of internal atom rearrangements occurring during thermal treatments, the challenge is to distinguish between the atoms by atom mobility in the particle and the large motion of atoms induced by the coalescence. Indeed, the NPs coalescence induces extended defects formation (high angle boundaries), which can act as nucleation center for chemical ordering, whereas in isolated particles, the temperature induces atoms rearrangements in surface or volume diffusion yielding the chemical order. The aim of our studies was to investigate the two kinetic mechanisms performing two kinds of experiments: **the in-temperature growth** of isolated nanoparticles to induce the internal atoms mobility in NPs (results already published²), and **the annealing** of RT-grown nanoparticles to induce the coalescence of separated NPs (these experiments).

In order to understand mechanisms leading to these morphological and structural changes, we have performed in situ and real time x-ray scattering measurements during the growth and the annealing of Co_xPt_{1-x} NPs at the UHV setup of ID03 beamline as previously demonstrated in BM32 SUV setup³. Grazing Incidence Small Angle X-ray Scattering (GISAXS) provides size, shape and correlation distance between NPs with the help of IsGISAXS software of R. Lazzeri. In addition, Monte Carlo simulations of relaxed cluster structures (ordered, disordered, fcc truncated octahedra, decahedra and icosahedra) have been performed using a semi-empirical tight-binding potential⁴, to compare with Grazing Incidence X-ray Diffraction (GIXD) experimental results obtained simultaneously with GISAXS measurements. To avoid purity problems and to control the interface

quality, Co and Pt atoms are deposited in-situ by condensation from UHV electron beam evaporation on weakly-interacting C/SiO₂ substrate.

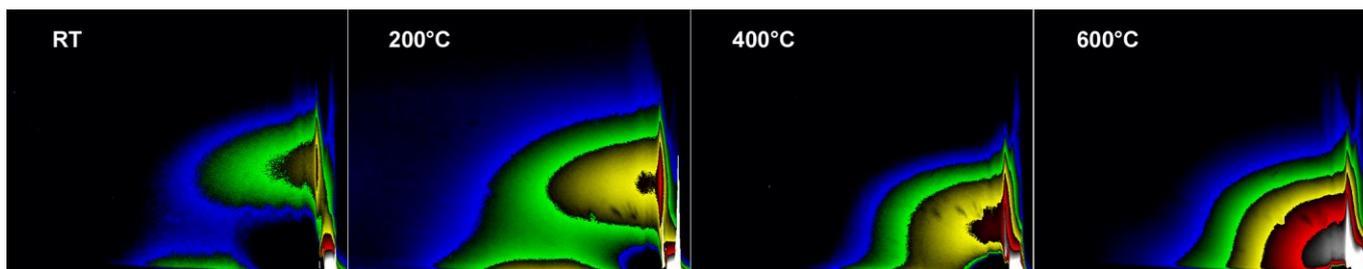


Figure 1: GISAXS pattern during the annealing of CoPt NPs at increasing temperatures.

Results:

Two samples prepared by equiatomic codeposition of Co and Pt metals and by successive deposition were followed by GISAXS and GIXD during their growth and annealing. For the codeposited sample, our results show that the evolution of the cluster structure is size-dependant or coalescence-dependant (Fig. 1). As previously demonstrated³, at room temperature, atom-by-atom growth conditions produce the non-equilibrium chemically disordered icosahedral Ih morphology almost exclusively. Quasi-static coalescence events at low annealing temperature (<300°C) don't lead to structural rearrangements, while at high temperature (400-500°C), annealing leads to the formation of decahedral morphology. Further annealing at 550°C and 600°C yields fcc disordered particles then partially chemical ordered nanoparticles (Fig. 2).

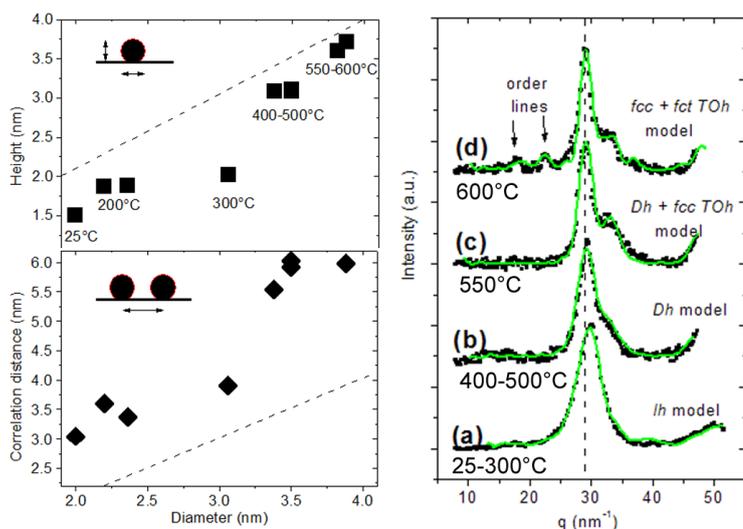


Fig 2 : The evolution of the nanoparticles shape parameters (diameter, height, interparticle distance) from GISAXS analysis and GIXD pattern evolution during the annealing

These results demonstrate that the growth kinetic mechanism traps the NP morphology in non-crystalline five fold atoms arrangements. Furthermore, the temperature assistance induces a coalescence mechanism which don't lead to a direct chemical ordering but to a progressive structural transition from icosahedral to fcc arrangements through a decahedral structure. Only from fcc chemically disordered structure, atom internal diffusion in the nanoparticles allows the transition to the L1₀ order. The elevated annealing temperatures promote the atoms diffusion, which is necessary to the ordering, but in the same time, increase the chemical disorder rate. This competition leads at 600°C to a partial ordering parameter of 30% in agreement with theoretical calculations⁴.

These structural and morphological transitions occur with the increase of the particle size from 2 to 4 nm and the temperature mainly above 400°C⁵.

For the successive deposition of Pt atoms followed by Co atoms deposition, the purpose was to construct an artificial core (Pt)-shell (Co) structure and to follow the critical competition at these particle size (1.3nm core) between the alloying mechanism (which is favoured by the high pair interaction energy) and the growth kinetic (which limits the atom mobility). The preliminary results show the feasibility of this kind of experiment and the possibility to evidence in real time, either alloying or segregation behaviour. The analysis of these combined GISAXS and GIXD shows the alloying of the nanoparticle surface in earlier stages, followed by the formation of a pure Co shell.

¹ J. Penuelas, C. Andreazza-Vignolle, P. Andreazza, A. Ouerghi, N. Bouet, **Surf. Science** 602, 545 (2008).

² J. Penuelas, P. Andreazza, C. Andreazza-Vignolle, C. Mottet, M. De Santis, H.C.N. Tolentino, **Eur. Phys. J.** 168, 19 (2009).

³ J. Penuelas, P. Andreazza, C. Andreazza, H.C.N. Tolentino, M. De Santis, C. Mottet, **Phys. Rev. Lett.** 100, 115502 (2008).

⁴ G. Rossi, R. Ferrando, C. Mottet, **Faraday Discuss**, 138 (2008).

⁵ P. Andreazza, C. Mottet, J. Penuelas, C. Andreazza-Vignolle, H.C.N. Tolentino, R. Felici, N. Bouet, in preparation.