

Non-equilibrium CoPt nanoparticles structural transitions or how the temperature assistance lead to tunable structures

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Co- and Fe-based magnetic nanoparticles (NPs) have attracted a lot of interest because of their applications in ultrahigh density recording media. In particular, FePt and CoPt NPs are especially promising due to the combination of size reduction and alloying effects, which induce large magnetic moment and high magnetic anisotropy [1].

In order to achieve suitable magnetic performances, at this nano-scale, subsequent thermal treatment, during or after the bimetallic NPs growth, is often required. This temperature assistance can lead to morphological changes or important chemical rearrangements in the NPs. Moreover, in case of supported NPs, this thermal treatment can modify the NPs size and dispersion on the substrate surface [2]. The present understanding of fundamental mechanisms, such as driving force for yielding specific NPs structures or morphologies, as well as structure-property correlations, has been hindered by the lack of knowledge of the precise atomic arrangement, especially in the case of few nanometers-size NPs. The challenge is to distinguish during the internal atom rearrangement induced by thermal treatments, between the atom-by-atom mobility and the large motion of atoms induced by the coalescence. Indeed, the coalescence between nanoparticles induces extended defects formation like high angle boundaries, which can act as nucleation center for fast structural transitions, like chemical ordering.

Supported CoPt NPs were studied in the 1-4nm size range by in situ and in real-time X-ray scattering measurements during their co-deposition growth and their annealing. These investigations were performed in UHV conditions at the European Synchrotron Radiation Facility (ESRF) on the BM32 SUV beamline. Grazing Incidence Small Angle X-ray Scattering (GISAXS) provides size, shape and correlation distance between NPs, while X-ray diffraction (GIXD) allows structure identification. In addition, Monte Carlo simulations of relaxed CoPt cluster structures (ordered or disordered truncated octahedral, decahedral and icosahedral) were performed using a semi-empirical tight-binding potential [3], to interpret diffraction experimental results.

Our results show that the evolution of the cluster structure is size-dependant or coalescence-dependant [4]. Dynamical coalescence events in the early stage (<300 atoms) of the growth at 500°C are the main responsables for the fcc NPs formation, while at room temperature, atom-by-atom growth conditions produce the non-equilibrium icosahedral Ih morphology almost exclusively. On the other hand, annealing (400-500°C) leads to the formation of decahedral rather than fcc morphology resulting of the quasi-static coalescence of Ih particles (>300 atoms). Further annealing at 600°C yields partially chemical ordered nanoparticles, by atom-by-atom internal rearrangements.

This opens a new understanding of the coalescence effect versus size effect on bimetallic particle structure transition with the temperature, in a 1-4nm size range.

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