**Ostwald ripening in nanoalloys: when thermodynamic drives a size-dependent particle composition**


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Metallic alloy clusters also called nanoalloys, are attracting increasing attention because of the immense technological potential that arises from combination of size effects with composition effects. However, the design of nanosystems with new and tuneable properties requires understanding the phenomena that influence cluster size and composition. Ostwald ripening is a major mechanism in the heat-induced size change of nanoparticles (NPs) on a substrate or in solution. This thermoactivated process was firstly described by the Lifshitz-Slyozov-Wagner theory [1]. When they receive energy in form of heat, larger particles are more energetically favored than smaller particles. Consequently, smaller clusters dissolve and the dissolved atoms redeposit on the surfaces of larger particles. However, this phenomenon becomes more complex when considering the coarsening of multi-element nanoparticles. Here, we have exploited the performances of both analytical microscopy and high resolution imaging to understand the atomic mechanisms involved in the coarsening of CoPt NPs. These TEM observations are explained within a thermodynamical framework.

Although NPs coarsening has been intensively studied, very little attention has been paid to the impact of this phenomenon on the composition of nanoalloys. We undertook EDS nano-analyses for simultaneously analyzing size and composition of single CoPt NPs, before and after annealing (1 hour at 750 °C). Figure 1 shows that the relative composition of CoPt NPs is strongly modified during annealing and displays a size-dependent behavior. Indeed, before annealing all the NPs are close to the equiatomic composition (± 5%). After annealing, the largest particles in a size range from 6 to 10 nm formed by the growth mechanisms, present a large excess of cobalt (68 ± 4 at.%), whereas particles below 3 nm present a lower cobalt concentration (45 ± 5 at.%). We have established a thermodynamic model to clarify the origin of this effect. The consistency of our theoretical and experimental results (Fig. 1) demonstrates that the size-dependent composition of nanoalloys measured after annealing, origins from the fact that the evaporation rate of atoms from particles is about a few orders of magnitude higher for Co than for Pt. Consequently, the system tends towards the thermodynamic equilibrium of Co atoms, because Co atoms have a higher mobility [2].

To provide the experimental evidence that the exchange of atoms between the NPs is faster for Co than for Pt, we performed a quantitative HRTEM analysis of single moving atoms by using the recently installed JEM-ARM200F microscope. The unique configuration of this microscope combining a cold-FEG and a CEOS aberration corrector for the objective lens is perfectly adapted to the fascinating study of single atom diffusion. Figure 2a shows that the quantitative analysis of single atom contrast, supported by image simulations, allows the chemical identification of single Co or Pt atoms diffusing on a very thin carbon film. This step forward in characterizing single atom diffusion revealed that during the beam-induced coarsening of CoPt nanoparticles, the exchange of atoms between the NPs is more important for Co than for Pt (Fig. 2b). Thus, this result confirms that the energy barrier for atomic evaporation from a NP to the substrate is higher for Pt than for Co, leading to faster Ostwald ripening for Co.

More importantly, compositional changes due to the multiple kinetics of Ostwald ripening are expected in all nanoalloys (binary and multicomponent nanoalloys) as soon as they contain species with different mobilities, as for example in AuPd NPs [3]. Therefore, the present work emphasizes the complexity of controlling together size and composition in nanoalloys, which is nevertheless crucial for understanding and exploiting their physical and chemical properties.
References


Figure 1. TEM images of CoPt NPs with the corresponding particles size distribution in insert. (a) As-grown NPs. (b) NPs after 1h at 750°C. (c) Single particle composition measured by EDS nanoanalysis, as a function of their size. Blue square: as-grown NPs. Red circle: NPs after 1h at 750°C. Black line: theoretical curve calculated in a thermodynamical framework [2].

Figure 2. Quantitative single atom imaging. (a) HRTEM image of CoPt nanoparticles on which single atoms are detected on the carbon film between NPs. The intensity profile 1 (right side) shows two Co atoms (signal to noise of 2.6 ± 0.3) whereas the intensity profiles 2 and 3 show two Pt atoms (signal to noise ratio of 3.4 ± 0.4). (b) Statistical analysis of signal to noise ratio of the single atoms detected on HRTEM images. This histogram shows that Co atoms are twice more frequently detected than Pt atoms.