Electronic Supplementary Information

Combined atomistic simulations to explore metastability and substrate effects in Ag-Co nanoalloy systems

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Synchrotron radiation experimental procedure

In-situ Grazing Incidence Small Angle X-ray Scattering (GISAXS) and Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) measurements were carried out at the SOLEIL Synchrotron in Gif-sur-Yvette, France, at the SIXS beamline [1,2]. The photon energies and the incidence angle were chosen to reduce the absorption-induced fluorescence effect and to optimize the analysis depth to some nanometers [3]. The sample detector distance was chosen for each x-ray energy to adjust the q range of the collected signal in the reciprocal space. All GIWAXS signals were collected with an XPAD 2D detector to scan the scattered intensity in a large reciprocal space area, while for the GISAXS measurements, the 2D Mar CCD detector was used and located in a fixed position in the small reciprocal space area close to the direct beam. The GISAXS and GIWAXS detectors were calibrated in terms of detection uniformity, spatially and energetically.

The geometry of the scattering data collection is defined at a fixed grazing incidence α_i [3,4]: The scattered intensity is recorded as a function of the out-of-plane angle α_f with respect to the substrate surface and of the in-plane angle $2\theta_f$ (Fig. S1). For GIWAXS, the exit angle α_f is fixed and the scan angle is $2\theta_f$. The components of the momentum transfer $\mathbf{q} = \mathbf{k_i} - \mathbf{k_f}$, (scattering vector) defined by the incident k_i and the scattered k_f wave vectors are $q_x = k_i (\cos\alpha_f \cos 2\theta_f - \cos\alpha_i)$, $q_y = k_i (\cos\alpha_f \sin 2\theta_f)$ and $q_z = k_i (\sin\alpha_f + \sin\alpha_i)$ in the laboratory frame, x and y in the surface substrate plane and z out-of plane (y perpendicular to the incident beam). For GISAXS, the intensity is recorded in q_y and q_z on the 2D detector.

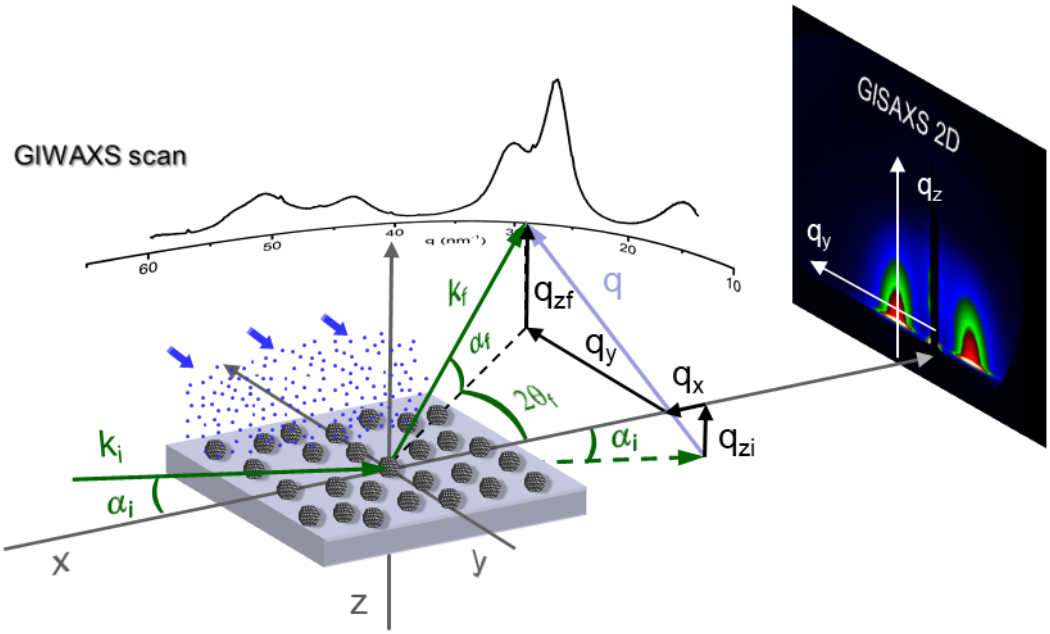

Figure S1: Strategy of the scattering data collection with an incident beam of wavevector $\mathbf{k_i}$, a scattered beam in the direction $\mathbf{k_f}$, with respect to the sample and the 2D GISAXS and 0D GIWAXS detection geometry (corresponding to q_z - q_y range, and q range profiles respectively).

Concerning the GISAXS data analysis: two cuts of intensity, *i.e.* 1D profiles, in the q_z and q_y, directions were extracted from a 2D GISAXS pattern as in Ref. [2]. The two perpendicular experimental cuts selected in the lobe intensity region (white lines) in Fig. S1 were simultaneously fitted with a dedicated code, the IsGISAXS software [4]. The simulations were made for a distribution of nanoparticles of weakly-truncated spherical shapes, to consider of the weak interactions between the deposited metals and the substrate [3,4]. According to the NPs organization on the substrate, the inter-particles correlation function was calculated using the Local Monodisperse Approximation (LMA), and a 1D-paracrystal organization model [4,5]. The adjustable parameters of the simulations were the NPs diameter D, the aspect ratio H/D (where H is the NPs height), the relative distribution of diameters σ(D)/D, the inter-particles distance Λ, and its standard deviation σ(Λ)/Λ [5].

Concerning the GIWAXS data analysis: the 1D experimental scattering profile was compared with simulated patterns obtained from a calculated model cluster on the basis of the Debye equation [2,6,7] and considering the set-up geometry using a dedicated custom software [8]. Preliminarily, a reference pattern from a substrate region without particle was measured in the same conditions, and was subtracted from the deposited nanoparticle sample pattern. The model clusters were obtained from molecular dynamics simulations with atomic displacements and chemical species exchanges of Co and Ag atoms in the canonical ensemble, using a semi-empirical potential as explained in the main text. A weighted sum of the intensities from several sizes or structures was used to fit the WAXS patterns considering the size distribution coming from GISAXS results [3].

Experimental investigation of Co deposition on Ag core

The in situ GIWAXS and GIWAXS results [2] reveal the time-resolved structural evolution during the Ag and Co depositions (see Fig. S2). For low amount of deposited Co atoms, we observe an incorporation of Co atoms over interatomic distances close to that of Ag, while the structure of the initial Ag particles is mostly kept as it is. At the highest amounts of Co, the Ag atoms lose their coherence, corresponding to a shorter distance order in the initial Ag domains, while domains of Co are created close to the interatomic distance of Co bulk (within 1% of the bulk lattice spacing). These observations from the initial Ag (average size of 1.9 nm) until a composition of about 70% Co atoms is reached, which reflect a progressive reduction of the coherence length in Ag domains and of the number of Ag neighbors, and also a higher local structural disorder, agree with a progressive formation of a core-shell Co@Ag particle by incorporation and agglomeration of Co atoms in the Ag nanoparticles.

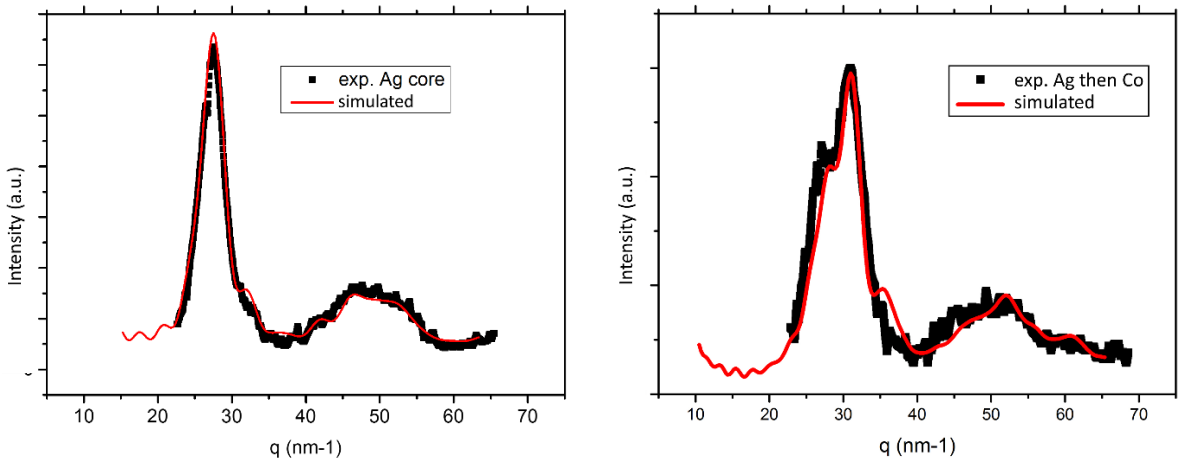

Figure S2 : GIWAXS spectra : (left) Initial Ag particle, and (right) Ag particle after Co deposition (until the AgCo2 composition), associated respectively with the simulated spectrum (red line) coming (left) from icosahedral distribution of Ag models centered on 309 atoms in size, and (right) from a Co-core/Ag-shell model of $Ag_{309}Co_{600}$ atoms.

Experimental investigation of Ag deposition on Co core

As previously, in situ scattering measurements showed that Ag nucleation does occur on the initial Co islands (average size of 1.7 nm), but does not lead to a core-shell configuration (see Fig. S3). After the deposition of Ag atoms on Co particles until about a composition of 40% Ag atoms, the GIWAXS measurements showed the formation of a silver domain associated with the initial Co core, as revealed by the GISAXS analysis of the size increase with the same density of particles. The kinetics of formation is most certainly the following: i) nucleation of Ag at the substrate/Co island interface, ii) growth of the Ag domain(s) on these nucleation sites, leading to a "pseudo-Janus" type configuration that minimizes the number of Ag-Co bonds that are energetically more unfavorable than Ag-Ag bonds. The presence of a substrate combined with kinetic considerations could be the origin of this behavior, and not only the immiscibility

between Co and Ag, that control the mechanism of Ag formation on Co islands leading to a final multidomain structure.

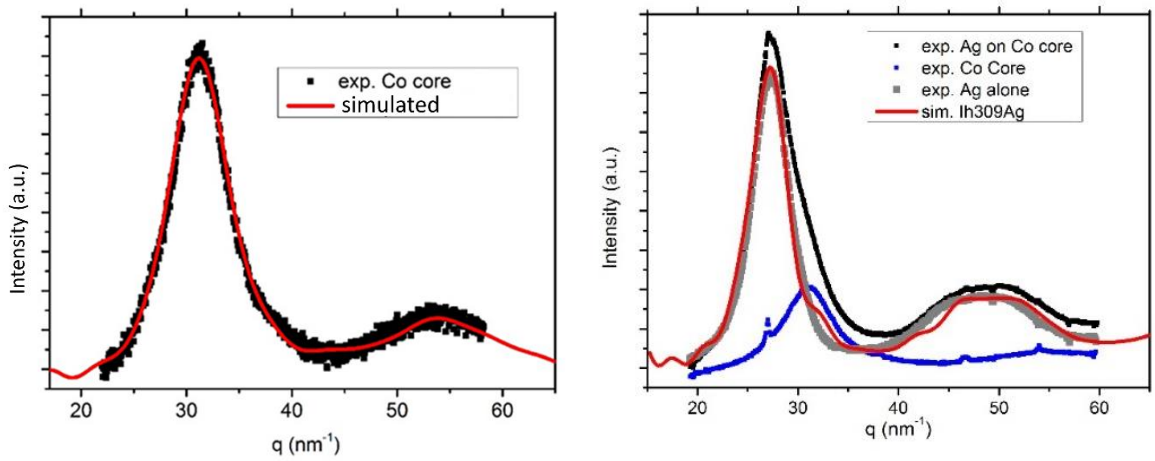

Figure S3 : GIWAXS spectra : (left) Initial Co particle, and (right) Co particle after Ag deposition (until the AgCo composition), associated respectively with the simulated spectrum (red line) coming (left) from amorphous and icosahedral distribution of Ag models centered on 1.7 nm in size, and (right) from the Co-Ag biparticle model with a Ag domain of icosahedral distribution of Ag models centered on Ag_{309} atoms.

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