A different balance of power between surface segregation and chemical ordering in Co-Pt and Pt-Ag nanoalloys.

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Ordering alloys are interesting systems due to the link between atom arrangement and properties, for instance in the field of catalysis for Pt-based alloys. In fact, Co-Pt system presents higher activity in the electrochemical oxygen reduction reaction than pure Pt [1], whereas Pt-Ag presents skills for plasmonic catalysis [2,3]. According to their bulk phase diagram, these systems are quite different; Co-Pt has three ordered phases ($L1_2$ at Co_3Pt and $CoPt_3$, and $L1_0$ at CoPt) while Pt-Ag holds one ($L1_1$ at PtAg) which is different from the one observed in Co-Pt. Moreover Silver presents a strong surface segregation tendency in Pt-Ag system whereas neither Co, nor Pt does in Co-Pt. The question arises if bulk ordering remains in nano-sized particles and how surface segregation accommodates chemical ordering. We propose here a theoretical study of surface segregation and chemical ordering.

Extending the study to the whole composition range of the Co-Pt and Pt-Ag alloys, we performed systematic Monte Carlo simulations in semi-grand canonical ensemble with semi-empirical many-body potential within the Second Moment Approximation (SMA) of the density of states which allows atomic relaxations. This potential has been fitted to ab initio calculations within the density functional theory. In the case of Pt-Ag, we use an additional Gaussian term within the SMA potential.

After the bulk phase characterization to check our interatomic potential, we characterized the surface segregation isotherms for Co-Pt semi infinite alloys with the (100), (110) and (111) [4] orientations to be compared to the surface segregation on the nanoparticle facets. We get a purely bidimensional phase $(\sqrt{3} \times \sqrt{3})R30(111)$, which is stable on nanoalloys when (111) facets prevail. The chemical ordering in the core of truncated octahedron clusters up to 3.3 nm can be nicely compared with the bulk phase diagram.

Contrary to the previous system, Pt-Ag presents a rather strong surface segregation which leads to a core-shell structure. Depending to the concentration, this structure can be ordered in the core.

References:
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