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► **To cite this version:**

Alexis Front, Christine Mottet. Trends of chemical ordering in Pt-based nanoalloys. Theoretical Chemistry Accounts: Theory, Computation, and Modeling, 2022, 141 (1), pp.2. 10.1007/s00214-021-02861-7. hal-03521317

HAL Id: hal-03521317

<https://hal.science/hal-03521317>

Submitted on 7 Feb 2022

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Trends of chemical ordering in Pt-based nanoalloys

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Received: date / Accepted: date

Abstract Nanoparticles of alloys represent a very interesting subject for fundamental research and, at the same time, a lot of usefull applications in industrial catalysis, microelectronics, sensors and medicine. Their properties depend on the atomic and chemical structure which has been the subject of intensive researches. This paper presents some trends in theoretical predictions of the chemical ordering and surface segregation in Pt-based nanosized systems, especially transition and noble metals for which catalytic, magnetic and optical properties are well known. By associating two different metals it is possible to improve selectivity in catalysis, or to increase magnetic anisotropy in magnetic systems, or to tune the surface plasmonic resonance in optical absorption, but the question is how the two species will mix or demix and how they will be distributed on the surface and in the core of the nanoparticle. This paper will give some general overviews concerning Pt-X, X=Co, Pd or Ag systems obtained from atomistic simulations. It will make a link between the chemical configuration adopted by the nanoalloys and the chemical characteristics of the system in terms of ordering tendency in bulk alloys and surface segregation in surface alloys.

Keywords Nanoparticles of alloys · Many-body potentials · Monte-Carlo simulations

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1 Introduction

Nanoparticles of alloys called nanoalloys met a large success in the past twenty years but they have been studied a longer time ago, before the birth of what we call now "nanoscience". Indeed, already in the seventies, the metallic clusters was mentioned by Jacques Friedel [1] as a new state of matter between molecules and crystal, and a very active field, with many potential applications from catalysis to photographic reactions. Jacques Friedel has probably inspired Fernand Spiegelman in two ways: not only because of his interest for clusters but also as a great defender of tight binding models, in solid state theory, to describe the energetics of many different systems. Fernand Spiegelman used such theory to describe single metals or noble metals, and recently, whereas density functional theory would like to keep being in the foreground, he developed in collaboration with Mathias Rapacioli, Nathalie Tarrat and coworkers the density-functional tight-binding method [2] which is at the frontier of the two approaches, also at the frontier between theoretical chemistry and physics. Whereas Jacques Friedel organized the first "International Symposium of Small Particles and Inorganic Clusters" (ISSPIC) in Lyon in 1976, before a long series of ISSPICs up to now, the second one has been chaired by Jean-Pierre Borel, in Lausanne, in 1980. Jean-Pierre Borel was the co-author with Philippe Buffat of the spectacular "size effect on the melting temperature of gold particles" [3], which was one of the first manifestation of the modification of physical properties with size. It inspired a lot of studies, both in theory and in experiments, where nanoparticles made of some tens to some thousands of atoms have shown fascinating properties as giant magnetic moments or superparamagnetism, surface plasmon resonance, higher catalytic properties than bulk phase. In the late nineties, I invited Fernand Spiegelman to join the jury of my PhD devoted to the study of mono and bimetallic nanoclusters by numerical simulations [4]. By associating two different metals in one nanoparticle it was possible to join all the advantages of the alloys with the specificity of the finite size effect. It has given rise to a large field of research from theory to application [5–7]. In the present review we will gather the results on three Pt-based systems with different chemical trends to show how the simple characteristics of the system can give reliable predictions on the chemical arrangement on nanoparticles and some guides for the phase diagrams of nanoalloys. The paper will be composed of four sections, including this introduction and the conclusion, the second section being devoted to the description of the energetic model and numerical simulations, and the third one to the results on the Pt-based nanoalloys i.e. Pt-Co, Pt-Ag and Pt-Pd in the shape of truncated octahedra.

2 Energetic model and numerical simulations

The theoretical approach is based on a semi-empirical potential derived from the electronic structure in the tight binding approximation: the so-called sec-

ond moment approximation (SMA) of the density of states which is fitted to *ab initio* density functional theory (DFT) calculations both for the pure metals and for the mixed interactions.

The SMA interatomic potential writes as follows [8] for an alloy with atom types *a* and *b*:

$$E_i^a = - \sqrt{\sum_{j, r_{ij} < r_{ab}^c} \xi_{ab}^2 e^{-2q_{ab}(\frac{r_{ij}}{r_{ab}^0} - 1)}} + \sum_{j, r_{ij} < r_{ab}^c} A_{ab} e^{-p_{ab}(\frac{r_{ij}}{r_{ab}^0} - 1)} \quad (1)$$

where the first term represents the attractive part with a square root dependence with the neighboring atoms and the second term, the repulsive part with a pairwise Born Mayer form. In this expression, r_{ij} is the distance between the atom at site *i* and their neighbors at site *j*, r_{ab}^c is the cut-off distance and r_{ab}^0 is the first neighbor distance depending on the nature of the atoms. Then, p_{ab} , q_{ab} , A_{ab} , ξ_{ab} are four parameters which can be fitted to the experimental or to the DFT values of lattice parameters, cohesive energies, surface energies, elastic constants for the pure metals and to the mixing energy or to the formation energies of ordered phases for the mixed interactions.

Then we use Monte Carlo simulations in the semi-grand canonical (S-GCMC) ensemble to optimize the chemical configuration on the clusters. Starting from truncated octahedral structure, we propose random atomic permutations and small random atomic displacements around each atom position. The difference between the two chemical potentials remains constant, together with the pressure, the temperature and the total number of atoms, and the concentration evolves toward the equilibrium concentration.

The Metropolis sampling ensures attainment of a Boltzmann distribution of the chemical configurations at equilibrium, this means when the number of Monte Carlo trials is sufficient to get reliable averages of physical quantities. In the Metropolis Monte Carlo, a trial is accepted if it lowers the total energy of the system. If not, it can still be accepted with the probability equal to $e^{(-\frac{\Delta E}{kT})}$ where ΔE is the energy difference between the configurations before and after the trial, k being the Boltzmann constant and T the temperature.

3 Pt-X nanoalloys with X=Co, Ag, Pd

These three systems present typical chemical tendencies: a strong ordering tendency for Co-Pt, no chemical tendency which means a solid solution in all the concentration range for Pt-Pd, and a phase separation tendency in the Pt-diluted Pt-Ag system but with a peculiarity to display one ordered compound at the equiconcentration. The mixing enthalpies of these systems are plotted in Fig. 1. The highest, in absolute value, the mixing enthalpy, the highest the tendency to form ordered compounds.

These general tendencies have a great impact on the chemical ordering on nanoalloys as we will show in the following.

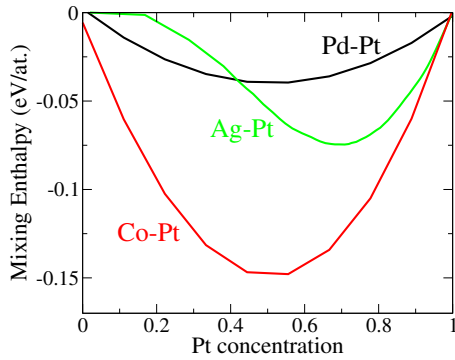


Fig. 1 Mixing enthalpies for the three different systems: Co-Pt, Ag-Pt and Pd-Pt. Experimental values from Hultgren et al. in *Selected Values of the Thermodynamic Properties of Binary Alloys*, American Society for Metals, Berkeley (1981) for Pd-Pt and Co-Pt systems, estimated values from Many-body potential fitted to ab initio calculations for Ag-Pt.

Let's start with the highest ordering tendency illustrated by the Co-Pt system. We performed Monte Carlo simulations in the whole concentration range of 1289 and 2951 atoms Co-Pt clusters. Some of the obtained configurations are illustrated in Fig. 2 where we can see typical ordered phases which are the one present in the bulk phase diagram. To characterize the ordered phases we plotted the occupation of the four fcc sublattices in the bulk and in the two cluster sizes. We observe in the bulk that the four sublattices are well separated in domains where at low Pt concentration the four sublattices are equally occupied, this means the phase is a disordered Co-rich solid solution. Then, one over four is fully occupied by Pt, the other three by Co, this corresponds to the L_{12} (Fig. 2-a) at 25% of Pt corresponding to the Co_3Pt compounds in bulk. This phase is made of an alternance of pure and mixed layers along the (100) direction. The domain of existence of this phase is extended up to around 40% of Pt. Then, two over four of the sublattices are occupied by Pt, the other two by Co, this corresponds to the L_{10} phase (Fig. 2-b) at equiconcentration corresponding to the CoPt compounds in bulk. This phase is made of an alternance of pure layers along the (100) direction and is stable in a domain of concentration between 40 and 60% of Pt. Then the same L_{12} phase but Pt-rich corresponding to the CoPt_3 compounds in bulk is stable in a domain between 60 and 80% of Pt (Fig. 2-c). Finally the four sublattices are equally occupied, this is the Pt-rich solid solution. The tricky thing when we pass from the bulk to the clusters is that in the cluster shape, the system have to accommodate the finite size with a given morphology, notably the coexistence of (100) and (111) facets, and possible surface superstructures which does not exist in bulk.

In fact, the core of the nanoparticles follows very well the different bulk ordered phases i.e. the L_{12} Co_3Pt and CoPt_3 , and the L_{10} CoPt as shown in Fig. 2. Concerning the facets, the (100) facets present the $c(2 \times 2)$ superstructure which is a simple prolongation of one (100) mixed layer of the L_{12} bulk ordered phase. Concerning the (111) facets, things are a little more compli-

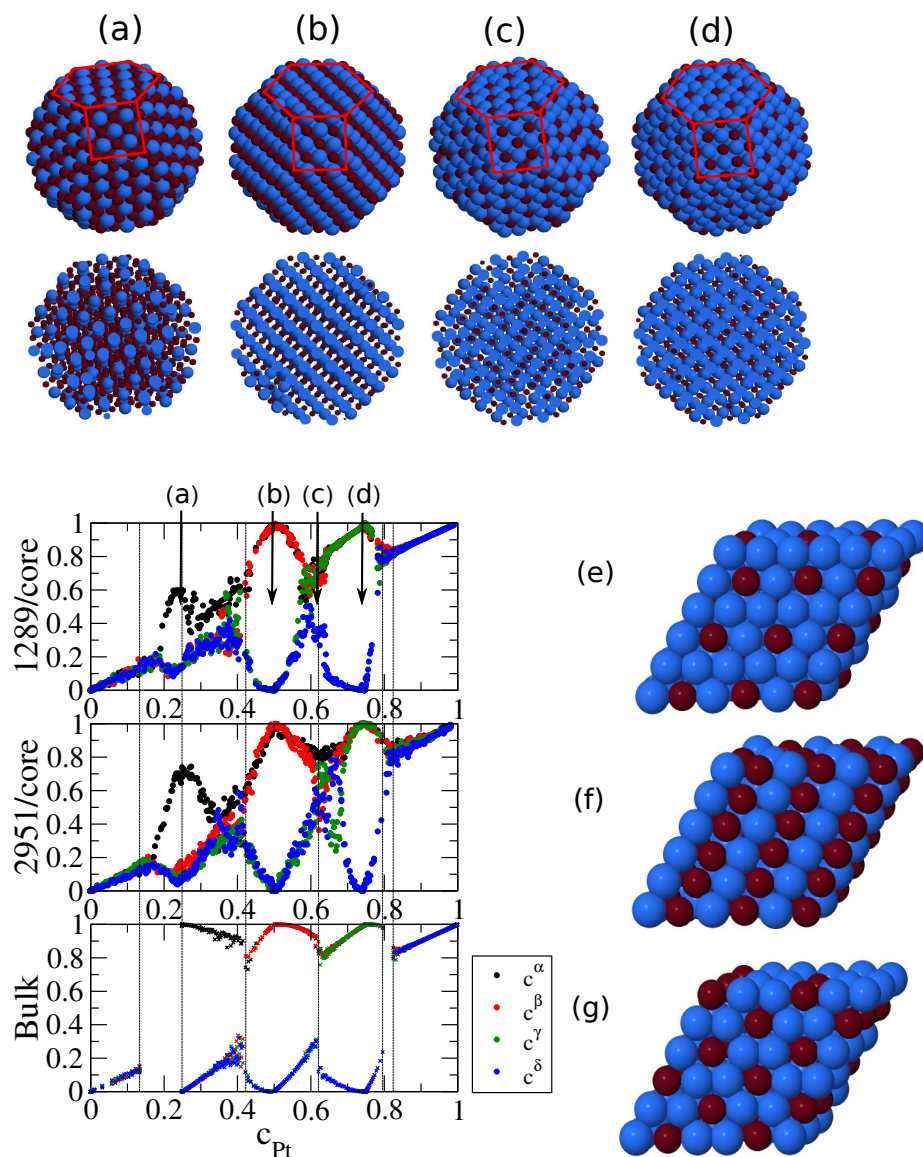


Fig. 2 Snapshots of the Co-Pt TOh nanoparticles with 25% (a), 50% (b), 66% (c) and 75% (d) of Pt (Co atoms in brown and Pt atoms in blue). The graphs represent the fcc sublattices occupations of the core of the TOh₁₂₈₉, the TOh₂₉₅₁ and the bulk alloy as a function of Pt concentration from ref. [9]. The pictures on the right represent the (111) surface reconstructions that we observe on the (111) facets of the clusters with the $p(2 \times 2)$ in (e), the $p(2 \times 1)$ in (f) and the $(\sqrt{3} \times \sqrt{3})R30^\circ$ in (g).

cated because as in the infinite Co-Pt surfaces [10], the Co-Pt (111) facets present the $(\sqrt{3} \times \sqrt{3})R30^\circ$ (Fig. 2-(g)) with a slight Pt enrichment at the surface as compared to the $p(2 \times 2)$ (Fig. 2-(a)) which is the proper structure in a (111) $L1_2$ layer with 1/4 or 3/4 of Pt. In the $(\sqrt{3} \times \sqrt{3})R30^\circ$, the concentration at the surface is of 33 or 66% whereas the core is around 25 or 75%. This slight surface segregation at the (111) facets of the cluster with the $L1_2$ core leads to a chemical desordering of this phase below the surface which can be seen by the dispersion in the sublattice occupation in the $L1_2$ domain for the 1289 atoms cluster (see Fig. 2). When the size increases, from 1289 to 2951 atoms, the core is sufficiently large to be relatively ordered and the subsurface contribution is less important. To conclude, this behaviour is exactly a chemical ordering frustration in the cluster because of finite size effect.

Now let's go on with the Pt-Ag system for which there is both an ordering tendency and a phase separation tendency in bulk alloys. Indeed the bulk alloy at equiconcentration forms the ordered $L1_1$ phase, made of an alternance of pure atomic layers along the (111) direction. But except these ordered phase, the phase diagram [11] presents large miscibility gaps between this ordered phase and the two diluted solid solutions. We notice also that the dissolution of silver in platinum is particularly limited (about 1-2% at 800 K) whereas it is larger on the other side (up to 20% of Pt in Ag). These are some peculiarity of the Pt-Ag system that we have well reproduced in our semi-empirical atomistic potential [12–14]. Now if we look at the chemical configuration of a truncated octahedron of 1289 atoms (TOh_{1289}) (see Fig. 3) we can get two different structures in competition: one with the perfect $L1_1$ ordered phase in the core and an atomistic surface shell pure in silver (designated by $L1_1@Ag$) or an other one with the same $L1_1$ phase in the core but limited by concentric shells of alternately Ag and Pt (designated by $L1_1@Pt@Ag$). We have shown in ref. [12] that the most perfect $L1_1$ phase is only stable for relatively small size (below one thousand of atoms). This leads to conclude to a reversed size-dependent stabilization of ordered nanophase. Indeed, we observed that by increasing the cluster size, the extension of the $L1_1$ nanophase in the core is accompanied by a strong stress on the silver atomic layers in the core, as illustrated in Fig. 3 by the red-orange colors. The structure can release this stress by the alternation of concentric pure atomic shells from the surface as shown by the structure $L1_1@Pt@Ag$. From the energetic point of view, this structure remains stable for larger sizes.

In that case we conclude that the chemical ordering in nanoalloys can be frustrated at larger size which is not the usual observation since in most of the finite systems, by increasing the size, we recover the bulk alloy properties. In the Pt-Ag system we have both an ordering and phase separation tendency, which means a tendency to form an ordered phase but also in the same time a tendency to surface segregation, which is a classical way to phase separate. By increasing cluster size, the ordered phase is limited by the coexistence of the two different driving forces: the ordering tendency leading to the $L1_1$ ordered phase in the core and the phase separation tendency leading to the Ag surface

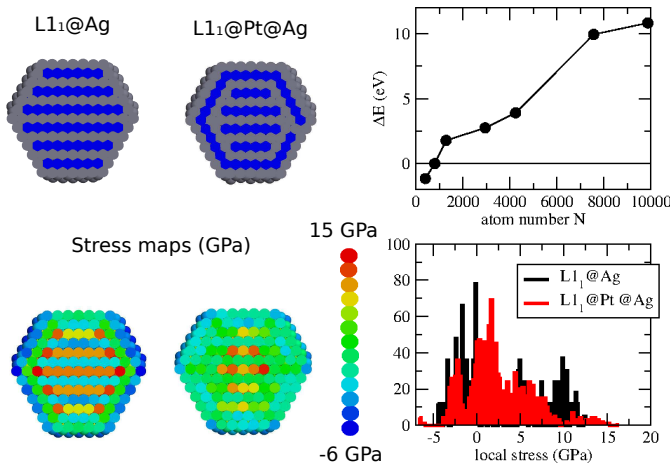


Fig. 3 Cutting views of the Pt-Ag TOh₁₂₈₉ (Pt atoms in blue and Ag atoms in grey) with different chemical arrangement: the L₁₁@Ag structure with a perfect L₁₁ core and a pure silver surface shell and the L₁₁@Pt@Ag one with a L₁₁ central core surrounded by Ag@Pt subsurface shells and a final silver surface shell. The color maps represent the equivalent stress map with a color scale from higher compressive stress in red to lower tensile stress in blue. On the right, the energy difference between the two different structure, a positive sign means the L₁₁@Pt@Ag is the most stable one. Finally the local atomic stress distribution for the two structures. All these results are taken from ref. [12].

segregation, these two effects resulting in an increasing stress with increasing size, which is defavorable to the well ordered L₁₁ phase.

Finally let us consider the Pt-Pd system where the chemical tendency is rather low, which leads to a solid solution all across the composition range in the bulk alloy. In the nanoalloys, we observe a Pd surface site segregation starting from the vertices, then the edges, then the (100) and finally the (111) facets. The hierarchy of the segregation follows typically the coordination number: the segregation starts at the less coordinated sites up to the highest coordinated ones. These segregation isotherms are plotted in the first column graphs in Fig. 4 for the two cluster sizes of 405 and 1289 atoms. In the second column, we plotted the Pd concentration on the different concentric shells starting from the surface up to the center. Even if there is almost no chemical ordering tendency in the Pt-Pd bulk alloy, in the clusters core we observe an alternance of pure Pd, pure Pt shells starting from the enrichment of the surface shell in Pd. This was already obtained by F. Calvo with similar model [16] on icosahedral structure that he called "onion-ring" structure. It has to be noticed that by increasing cluster size, the concentric alternative layers concern only the surface neighborhood and are not propagated in the core as shown by DeClercq et al. [15] and as we can see on Fig. 4 for the 1289 atoms size for which the central shells are mixed. Only the surface shell, the subsurface and the shell 1 are alternatively filled with Pd or Pt atoms. This onion-ring structure at the vicinity of the surface is a result of a slight tendency to Pd surface segregation because it has a lower surface energy.

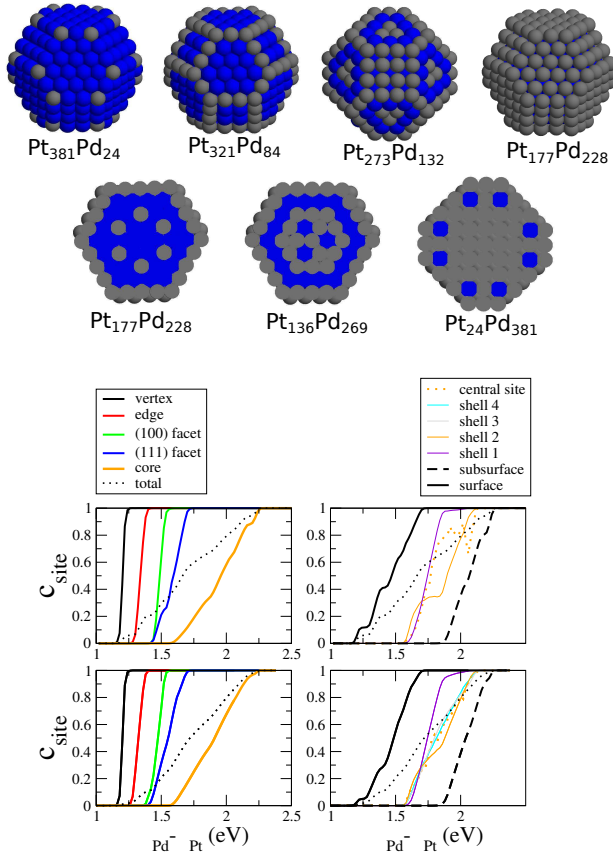


Fig. 4 Snapshots of a 405-atom truncated octahedra of Pt_NPd_M at 100 K (Pt in blue and Pd in grey) and the corresponding segregation isotherms as a function of the chemical potential for the TOh_{405} (first row) and for the TOh_{1289} (second row) for the surface sites and the concentric core shells, taken from ref. [15].

4 Conclusions

Looking at three different Pt-based nanoalloys we described very different chemical arrangements that can be linked to their bulk alloy characteristics. In the case of a strong ordering tendency as the Pt-Co system, we find that the truncated octahedron cluster displays the ordered phases as in the bulk with some surface reconstructions on the (111) facets which are also the ones predicted on the (111) infinite surface [10]. It is the $(\sqrt{3} \times \sqrt{3})R30^\circ$ which represents a slight Pt surface segregation of 0.33 or 0.66 depending on whether we are in the Co-rich or Pt-rich side, to be compared with the $p(2 \times 2)$ surface ordering at 0.25 and 0.75 with the same stoichiometry at the surface and in the bulk. In finite size systems, this surface reconstruction leads to a slight

chemical desordering in the layers below the surface which is more visible as the cluster size is small. Despite experimental studies on these systems, which clearly show the core ordering at equiconcentration [17–19], there is no precise determination of the surface chemical ordering which is out-of-reach by actual experimental tools.

For a system with both chemical ordering and phase separation tendency, depending on the concentration, things are different. This is the case of the Pt-Ag system for which there is a strong Ag surface segregation that enters in competition with the core ordering according to the $L1_1$ phase at equiconcentration as in the bulk. Such behaviour has clearly been observed by High resolution Transmission Electron Microscopy [12]. By increasing the size, the $L1_1$ core with the Ag pure surface shell becomes too much stressed because the rhombohedral deformation associated to the $L1_1$ phase is constrained by the silver shell. The cluster can release the stress by filling a subsurface shell with Pt with a lower atomic radius, which is not accessible by experiments up to now. However we demonstrated a reversed size-dependent stabilization of ordered nanophases [12].

Finally, for a system with no particular phase ordering or phase separation tendency, which means a solid solution in all the composition range as the Pt-Pd system, we show that nanoclusters display a local onion-ring structure, localized near their surface, and a solid solution in their core.

To conclude, the nanoalloys chemical arrangements can be rich and various and it is of prime importance to control the distribution of the different species in the system in order to optimize the physical and chemical properties of these nanoobjects which find more and more applications for industrial or medicinal purposes.

Acknowledgements The authors warmly thank Bernard Legrand, Guy Tréglia and Riccardo Ferrando for fruitful discussions and acknowledge support from the International Research Network-IRN "Nanoalloys" of CNRS. This work was granted access to the HPC resources of IDRIS under the allocation 2017-096829 made by GENCI.

Conflict of interest

The authors declare that they have no conflict of interest.

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