# Formation of a Surface–Sandwich Structure in Pd-Ni Nanoparticles by Interdiffusion: Atomistic Modelling

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## 1. Introduction

Bimetallic Pd-Ni nanoparticles are currently attracting a great deal of interest due to their physical and chemical properties, which are determined by their size, shape, structure and composition. In particular, it is well-known that Pd is a metal with important existing and potential applications as a catalyst in heterogeneous catalysis. The use of Pd as a single active metal component in catalysis has received considerable attention on the basis of its remarkable activity for oxidation reactions and the availability of cleaner fuels, but at the same time it has negative economical aspects due to its high cost [1]. An interesting approach in these respects consists of alloying Pd with lower cost and higher surface energy metals, since it would be economically attractive to design bimetallic catalyst nanoparticles in which the precious and catalytic Pd atoms segregate to the surface. Promising results in this sense have been obtained by using Ni [1-3].

Understanding and controlling of the atomic structure of alloy nanoparticles are important in both fundamental science and technological applications. Atomistic simulation techniques such as molecular dynamics (MD) have become a powerful tool in the field of nanotechnology by providing physical insight in understanding phenomena on an atomic scale and predicting many of the properties of nanomaterials.

In the present study, long–time scale molecular dynamics simulation in combination with the embedded atom method is used to investigate the effect of surface segregation phenomena on the atomic structure of Pd alloy nanoparticles (of diameter of $\sim$ 4.5 nm) containing $\sim$ 30 at. % Ni.

## 2. The model

A spherical core–shell f.c.c. structure was chosen as the initial state for bimetallic Pd–Ni nanoparticle wherein a core of Ni atoms is surrounded by shell of Pd atoms. Then the static relaxation procedure was applied to accommodate the core and shell atoms especially at interface, since Pd atoms (the equilibrium bulk lattice constant is 3.89 Å) are noticeably larger than Ni atoms (the equilibrium bulk lattice constant is 3.52 Å) with difference in atomic sizes of $\sim$ 10%. Following this, atoms were given initial velocities according to the Maxwell distribution at the temperature of 1000 K and the MD procedure of isothermal annealing was performed. The MD procedure consisted of a numerical integration of the equations of atomic motion according to the Verlet algorithm with a time step $\Delta t$=1.5 fs. Periodically without an effect to the continuity of the annealing procedure the system was transferred to a state at $T$=0 K where atoms occupied equilibrium positions in local potential minima by making use of the static relaxation method. After this, the atomic movements and structure transformations occurring in the model were analyzed.

## 3. Results and Discussion

It is found that such nanoparticles form a surface–sandwich structure by interdiffusion. In this structure, the Ni atoms, which mostly accumulate in a layer just below the surface, at the same time are located in the centres of interpenetrating icosahedra and generate a subsurface shell as a Kagome net. Meanwhile, the Pd atoms occupy the vertices of the icosahedra and cover this Ni layer from inside and outside as well as being located in the core of the nanoparticle forming a Pd–rich solid solution with the rest of the Ni atoms. A basic structure of such nanoparticles nucleating during interdiffusion in the system is a Ni spherical subsurface shell (layer) having a structure of the Kagome net with 'sequence faults' (see Fig. 1). Each Ni atom of the spherical subsurface layer almost always has 4 Ni and 8 Pd nearest neighbours. It should be noted that planar layers of Kagome nets are the basic structure of the well–known bulk Frank–Kasper phases of certain intermetallic alloys.
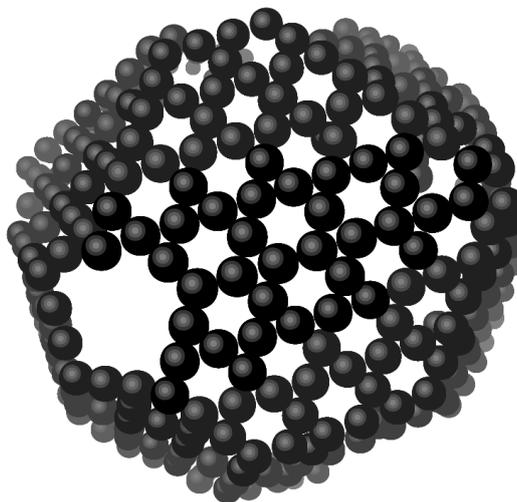


Fig. 1. Snapshot of the Ni subsurface shell having a structure of the Kagome net with 'sequence faults' after ~0.3 $\mu$s of annealing at $T = 1000$ K. Every Ni atom of the subsurface shell is located in the centres of interpenetrating icosahedra and almost always has 4 Ni and 8 Pd nearest neighbours. For better clarity only a half of the shell and only Ni atoms at centres of icosahedra are shown on the perspective projection with size and grey-scale graduation.

## 4. Conclusion

Long–time scale molecular dynamics simulation in combination with the embedded atom method has been used to investigate the effect of surface segregation on the atomic structure of Pd alloy nanoparticles (of diameter of ~ 4.5 nm) containing ~ 30 at. % Ni. We have found that such nanoparticles form a surface–sandwich structure where the Ni atoms, which mostly accumulate in a layer just below the surface, at the same time are located in the centres of interpenetrating icosahedra and generate a subsurface shell as a Kagome net. Meanwhile, the Pd atoms occupy the vertices of the icosahedra and cover this Ni layer from inside and outside as well as being located in the core of the nanoparticle forming a Pd–rich solid solution with the rest of the Ni atoms.

## References

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