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Structure, energetic and phase transition of multi shell icosahedral bimetallic nanostructures: A molecular dynamics study of Ni_mPd_n ($n + m = 55$ and 147)

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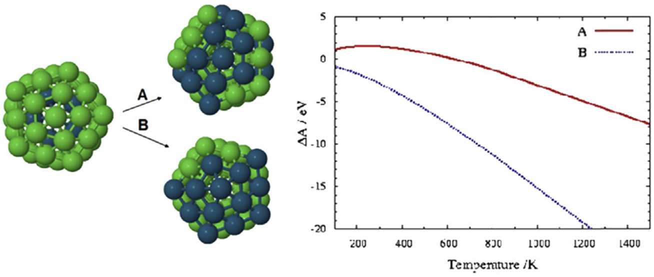
HIGHLIGHTS

- Nanostructures of Ni_mPd_n clusters for $m + n = 55$ and 147 have been studied.
- Structures favor the formation of nickel-core surrounded by palladium atoms.
- In general, it appears the increase of cohesive energy with the nickel composition.
- Calculated thermodynamic parameters confirm the energetic results.
- Results show also the palladium segregation on the surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Structure, energetic and thermodynamic properties of multi shell icosahedral bimetallic nickel–palladium nanostructures with the size of 55 and 147 atoms were studied by using the molecular dynamics simulations and the microcanonical ensemble version of multiple histogram method. In 55 atoms icosahedra, two core–shell motifs, $Ni_{13}Pd_{42}$ and $Pd_{13}Ni_{42}$ with their isomers $Pd_{13}(Pd_{29}Ni_{13})$ and $Ni_{13}(Ni_{29}Pd_{13})$ were considered. Similarly in 147 atoms icosahedra, all mutations corresponding to the occupations of either nickel atoms or palladium atoms in the core, inner shell or outer shell and their isomers generated by interchanging thirteen core atoms with thirteen atoms of the other type in the inner and outer shells were considered. It is found that the nickel-core clusters are more stable than the palladium-core clusters and cohesive energy increases with the nickel composition. Phase transition of each cluster was studied by means of constant volume heat capacity. The trend in variation of melting temperature is opposite to the energy trend and special increase in melting points was observed for nickel-core isomers compared to the palladium-core isomers. Helmholtz free energy change with temperature for shell to core interchange of thirteen atoms revealed the thermodynamic stability of the formation of $Ni_{core}Pd_{shell}$ structures and the surface segregation of palladium.

1. Introduction

Mixed clusters offer more possibilities for tunable properties than homogeneous clusters, since not only the size but also the stoichiometry and the spatial distribution of the components can vary. Experimental studies reported by Bansmann et al. [1] have

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shown the enhancing magnetic properties of binary alloy clusters such as FePt, FeCo, CoPt, CoAg. Low energy ion spectroscopy (LEIS) experiments carried out on Ni/Ag and Pt/Ag clusters by Cottancin et al. [2] have shown that the cluster surface is entirely covered by silver atoms for the two systems. In theoretical studies, the Aguilera-Granja group [3,4] has reported the influence of the chemical order on magnetism and metallic behavior of the Pd–Co system, and magnetic moment of verities of Fe_mY_n nanoalloys. Reetz et al. [5] produced transition metal clusters stabilized with tetraalkylammonium salts by size-selective electrochemical preparation technique. Products confirmed by single-particle energy-dispersive X-ray emission spectroscopy were in the 2.5–3.5 nm size range. Elemental analysis and transmission electron microscopy were used to measure the metal content. Studt et al. [6] have recently reported their work on “Non-precious metal alloy catalysts for selective hydrogenation of acetylene” in *Science* magazine. In addition to the potential applications of clusters and nanostructures in nanoelectronic memory devices and catalysts, they are very important in homogeneous nucleation, crystal growth, and understanding the structure of amorphous materials. Physical properties of metallic clusters depend also on temperature and energy.

Extensive literature survey revealed that little attention has been paid to nickel–palladium system (Ni/Pd) in spite of its chemical and technological important. In experimental studies, Reetz et al. [7] have shown that palladium/nickel bimetallic clusters are very effective catalysts for phosphine-free Suzuki and Heck reactions and Pachón et al. [8] have shown that not only core–shell Ni–Pd clusters are active in Hiyama cross-coupling, but they are also superior to the monometallic and bimetallic alloy structures.

Manago et al. [9] prepared palladium-coated nickel particles by electroless plating of palladium ions onto preformed nickel particles. In situ magnetometry and XRD investigation under an H_2 atmosphere were performed and particles were found to consist of a ferromagnetic nickel core surrounded by ferromagnetic and paramagnetic palladium.

In theoretical studies, out of Ni, Ag and Pd, Ni/Ag and Ag/Pd systems have been drawn much attention compared to the Ni/Pd system [10–15]. Guevara et al. [16] investigated the magnetic properties of the clusters up to 561 atoms with variable Ni/Pd compositions assuming the $Ni_{core}Pd_{shell}$ cuboctahedral configuration. Their electronic structure calculation found an enhancement of the average magnetic moment of the nickel atoms above that of the bulk. Wang et al. [17] also found similar enhancement of magnetism in $Ni_{core}Pd_{shell}$ clusters.

Temperature effects cause significant changes in the stability, structure and physical properties of finite system compared to the bulk. Therefore understanding the temperature effect is essential for any technological application. Apart from the electronic properties obtained from electronic structure calculations, thermodynamic properties of clusters are mainly investigated by applying either the Monte Carlo or Molecular dynamics techniques. Recently Nieves-Torres et al. [18] used the Monte Carlo simulated annealing (MCSA) technique to investigate the phase transitions of two-dimensional seven atoms and three-dimensional thirteen atoms Ni/Pd clusters. Hewage [19] investigated the dynamic and thermodynamic properties of thirteen particle icosahedral nickel–palladium clusters by using the molecular dynamics and histogram methods.

In this paper, results on the structure, energetic and phase transition of multi shell icosahedral Ni_mPd_n ($n + m = 55$ and 147) clusters will be discussed. We explicitly selected the icosahedral geometry based on previous reports that the icosahedra and polyicosahedra are more favorable for nanoalloys especially because small atoms can be accommodated inside the cluster to reduce the compressive strain [14].

2. Interaction potential and calculation methods

In this study, metal–metal interactions were modeled using the Sutten–Chen potential [20] which is the extended version of the original Finnis–Sinclair pair potential [21] to represent all pair wise interactions: Pd–Pd, Ni–Ni, and Pd–Ni. Finnis and Sinclair potential in Eq. (1) includes two terms; the first term is to represent the repulsion between atomic cores and the second is to represent the bonding energy due to electrons. The potential has the form

$$U = \sum_{ij} U(r_{ij}) + \sum_{i} u\sqrt{\rho_i}, \tag{1}$$

ρ_i of the second term is the local density of atom. In the Sutton–-Chen's potential in Eq. (3), local density is given by

$$\rho_i = \sum_{j} \left(\frac{a}{r_{ij}}\right)^m, \tag{2}$$

and the pair repulsion is included by a reciprocal power so that the complete potential is

$$U = \varepsilon\left[\sum_{ij}\left(\frac{a}{r_{ij}}\right)^n - C\sum_{i}\sqrt{\sum_{j}\left(\frac{a}{r_{ij}}\right)^m}\,\right]. \tag{3}$$

This is truly a many body potential, but the force on each atom can be expressed as a sum of pair-wise contributions.

$$F_i = \sum_{j} F_{ij}, \tag{4}$$

where

$$F_{ij} = \varepsilon\left[n\left(\frac{a}{r_{ij}}\right)^n - \frac{Cm}{2}\left(\rho_i^{-1/2} + \rho_j^{-1/2}\right)\left(\frac{a}{r_{ij}}\right)^m\right]\frac{r_{ij}}{r_{ij}^2} \tag{5}$$

here, r_{ij} is the distance between ith and jth atoms. ε is a parameter with the dimensions of energy, a is a parameter with the dimensions of distance and C is a positive dimensionless parameter. These three parameters are not independent and are completely determined by the equilibrium lattice parameters and lattice energy of the face-centered lattice. Table 1 shows the parameters used in this calculation for neat palladium and nickel atoms given by the Sutton and Chen [20]. Parameters corresponding to interactions between different atoms (Ni and Pd) were predicted by using the combination rules. The geometric mean was used to obtain the energy scaling parameter and an arithmetic mean was used for n, m, and a.

Molecular dynamics simulations of a variety of multi shell clusters (Ni_mPd_n for $n + m = 55$ and 147) were performed by solving the classical equations of motion using the predictor corrector algorithm due to Gear [22,23]. The fifth order scheme was used to treat translational motions. Initial positions of mixed clusters were taken from positions of atoms in a quenched icosahedral structure. The linear velocities of atoms were then chosen randomly from the

Table 1
Parameters corresponding to the dimers of palladium, and nickel atoms used in the Sutton–Chen interaction potential model [20].

	n	m	ϵ/eV	C	a
Ni	9	6	1.5707×10^{-2}	39.432	3.52
Pd	12	7	4.1790×10^{-3}	108.27	3.89