Computational and Theoretical Chemistry 1059 (2015) 60–67

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

The study of dynamics and phase transitions of small Ag/Pd motifs using molecular dynamics and histogram methods

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ARTICLE INFO

Article history:
Received 22 October 2014
Received in revised form 13 January 2015
Accepted 10 February 2015
Available online 5 March 2015

Keywords:
Nanostructures
Computer modeling and simulation
Molecular dynamics
Phase transitions

ABSTRACT

The structural and thermodynamic properties of bimetallic $Pd_nAg_{(13-n)}$ ($n \leqslant 13$) have been carried out using the Molecular Dynamics (MD) with Sutton–Chen potential and histogram methods, respectively. Thirteen particle icosahedral clusters of neat palladium and silver atoms were first reproduced accordingly with the results in literature. Then in the silver icosahedra, each silver atom has been successively replaced by palladium atom. Calculation is repeated for both palladium-centered and silver-centered clusters. It is found that the palladium-centered clusters are more stable than the silver-centered clusters and cohesive energy increases along the silver end to palladium end. Phase transition of each cluster species is studied by means of caloric curve, root mean square bond fluctuation and heat capacity. Trend in variation of melting temperature is accordance with the energy trend. Silver centered cluster shows a premelting at low temperature due to onset of more facile motions of center particle (silver) and a transformation to a low energy palladium-centered configuration in the cluster depending on the cluster compositions. Species-centric order parameters and velocity autocorrelation functions are used to understand the dynamic behavior in the solid and liquid phases. Mixing of silver–palladium occurs in the liquid phase with higher silver concentration and palladium-core/silver-shell cluster formation would occur at low silver concentration.

1. Introduction

We recently reported the dynamics and phase transitions patterns of thirteen particles icoshahedral Ag/Ni [1], Ni/Pd [2] and the multi shell icosahedral nanostructures of Ni_mPd_n ($n + m = 55$ and 147) [3]. Recent attention on bimetallic nanostructures especially made of Ag, Ni and Pd is due to the wide range of their applications in technology, catalysis, medicine, and hydrogen separation and storage due to distinct electronic and chemical properties from those of their parent metals [4,5]. Specifically, Ag/Pd alloys have attracted much attention in many areas of science in recent years. Amandusson et al. [6] has revealed a considerable permeation rate in Ag–Pd hydrogen separation membranes. These alloys have also been used as selective hydrogenation catalysts [7–9] and electrocatalysts for both the anode and cathode of direct fuel cells because of their better catalytic properties and lower cost than Pt-based catalysts [10,11].

In experimental studies, it is extremely difficult to vary the size and the spatial distributions of the components freely whereas in computer simulation, we can model various structures and check for properties especially dynamics and thermodynamics of phase transition. Several computational methods such as electronic structure calculations [12–15], generic algorithms [16–18], Monte Carlo [19,20] and molecular dynamics [21,22,4,23] methods have been used to investigate the most stable structures of bimetallic clusters. In comparison on these methods, electronic structure calculation is a challenging task for transition metal system due to the complexity of their potential energy landscape and the complexity increases further in bimetallic alloys [24]. As a result, in optimization process, system may optimize to local minima instead of desired global minimum. On the other hand, the genetic algorithm is suitable for producing the final global minimum cluster morphology, but bimetallic clusters which are experimentally synthesized as the solid solution cannot be explained [25,26]. Similarly, considering the Monte Carlo method, it fails to account the dynamics properties and also calculation involves in the constant temperature despite the fact that an isolated cluster evolves at constant energy. Instead, molecular dynamics technique is more capable of locating and passing local minima to locate the global structure and the same time it allows drawing the thermodynamics parameters.

Temperature effects cause significant changes in the stability, structure and physical properties of finite system compared to the bulk. Both experimental and theoretical studies have shown

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http://dx.doi.org/10.1016/j.comptc.2015.02.002
2210-271X/

the decrease of the melting temperature with the reduction of the cluster diameter [27–30]. Therefore understanding the temperature effect is essential for any technological application. Apart from the electronic properties and structural properties obtained from electronic structure calculations and generic algorithms technique, thermodynamic properties of clusters are mainly investigated by applying either the Monte Carlo or Molecular dynamics techniques. Recently Nieves-Torres et al. [19] and Cheng et.al [20] 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 and the composition effect on the melting processes of the 55-atom icosahedral Ag/Pd bimetallic clusters, respectively. In our previous papers [1,2], we reported the use of the molecular dynamics and histogram methods to calculate the thermodynamic properties of thirteen particle icosahedral Ni/Ag and Ni/Pd cluster systems. In this paper, results on the structure, energetic, dynamics and phase transition of small icosahedral Pd_mAg_n ($n + m = 13$) clusters will be discussed. We explicitly selected the icoshahedral 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 [31]. Icoshahedral thirteen particle system can be considered to be the smallest core–shell system which has a central position (core) surrounded by 12 outer positions (shell) and hence mimics the properties of larger bimetallic systems.

2. Interaction potential and calculation methods

In this study, metal–metal interactions were modeled using the Sutten–Chen potential [32] which is the extended version of the original Finnis–Sinclair pair potential [33] to represent all pair wise interactions: Pd–Pd, Ag–Ag, and Pd–Ag. Complete details of parameters are given in Table 1 and application to the current system can be found elsewhere [2].

Molecular dynamic simulations of a variety of mixed clusters of $Pd_nAg_{(13-n)}$ for $n \leqslant 13$ were performed by solving the classical equations of motion using the predictor corrector algorithm due to Gear [34,35]. 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 Boltzmann distribution. All motions were reset with respect to the center-of mass of the cluster. The typical time step of 10^{-15} s yielded energy conservation is about a part in 10^4 over about 10^6 steps (typical simulation time of 1 ns).

As in all straightforward MD calculations, a trajectory at a given energy yields equilibrium information and calculated using standard averaging techniques [36,37]. Stable structures (local minima) for a given cluster are found by extracting the positions of atoms of the trajectory at regular time intervals, and using these data as the staring points for a conjugate gradient minimization procedure [38–40].

2.1. Caloric curves, rms bond fluctuations and velocity autocorrelation function

The temperature fluctuates throughout the constant energy MD simulation. Therefore temperature should be calculated averaging the kinetic energy, E_{kin}, given by,

$$E_{Kin} = \frac{1}{n_t}\sum_{j=1}^{n_t}\left[\sum_{i=1}^{n}\frac{p_i^2}{2m_i}\right], \tag{1}$$

where n_t is the total number of time steps, p_i is the linear momentum of the ith particle, n is the number of atoms and m_i is the atomic mass of the each ith atom. All kinetic energies are calculated with respect to the center of mass of the cluster. Then the kinetic temperature is given by,

$$T = \frac{2E_{\text{kin}}}{N_{\text{tot}} - 6}, \tag{2}$$

where N_{tot} is the total number of degrees of freedom. Since the overall cluster translations and rotations are frozen, six degrees of freedom are excluded from the total.

The connection between cluster melting, phase transitions in finite clusters, and the *caloric curve* has been investigated by a number of authors [41–43]. The caloric curve is a graphical representation of a functional relationship between the mean kinetic temperature given by Eq. (2) and the total energy of the system. The shape of the caloric curve in the transition region has been reported either as a loop which connects the low energy side of the curve (hot solid) to the high energy side (cold liquid), or as having an inflection point as seen in this study. Loop behavior would only be seen if there is a large energy gap between the ground state and excited states [44]. It is also more likely in low-dimensional systems (very small clusters) [45].

Correlations of features observed in the caloric curve and those in the root mean square bond fluctuation parameter, δ, defined in Eq. (3), are two of the standard ways of identifying melting temperature [42,46]

$$\delta = \frac{2}{N(N-1)}\sum_{i,j}\frac{\left(\langle r_{ij}^2\rangle_t - \langle r_{ij}\rangle_t^2\right)^{1/2}}{\langle r_{ij}\rangle_t}. \tag{3}$$

Here N is the total number of atoms and r_{ij} is the bond distance between atoms i and j.

The velocity autocorrelation function, $C(t)$, given by Eq. (4) also gives the information on the motion of the atoms in the cluster. In solid-like clusters, the motion of the atoms is highly correlated and $C(t)$ exhibits oscillations as a function of time. In liquid-like clusters, the oscillations in $C(t)$ are completely lost which indicates an uncorrelated motion of the atoms in the cluster [47,48].

$$C(t) = \frac{\sum_{j=1}^{n_t}\sum_{i=1}^{n} v_i(t_{0j}+t)(v_i(t_{oj}))}{\sum_{j=1}^{n_t}\sum_{i=1}^{n} v_i^2(t_{oj})}. \tag{4}$$

2.2. Histogram method and thermodynamics

The fundamental quantity for studying the thermodynamics of a finite system is the classical density of states, $\Omega(E)$. This is the key to calculate all the thermodynamics quantities in both canonical and microcanonical ensembles. Histogram methods for determining densities of states or partition functions originate with Bennett [49] and others [50] but Labastie and Whetten were the first to use the multiple histogram method to investigate the thermodynamics of rare gas clusters [51]. Amar and Weerasinghe [52,53] supplemented histogram methods with an adiabatic switching procedure [54] to determine the absolute densities needed to study the kinetics of evaporation using phase space formalism. In the present study, the microcanonical ensemble version of the method developed by Calvo and Labastie [55] is used to calculate the thermodynamic quantities, especially the heat capacity

Table 1
Parameters corresponding to the dimers of palladium and silver atoms used in the Sutton–Chen interaction potential model [32].

	n	m	ϵ (eV)	C	a (Å)
Ag	12	6	2.5415×10^{-3}	144.42	4.09
Pd	12	7	4.1790×10^{-3}	108.27	3.89