Numerical Simulation of the Elastic Properties of Rh-20at%Pd Nanowire

J. Davoodi and M. J. Moradi

Abstract—**The aim of this research was to calculate Yong modulus, Bulk modulus and the elastic constants of Rh-20at%Pd (atom percent) nanowire. The molecular dynamics simulation technique was used to calculate the mechanical properties at constant temperature, constant pressure ensemble. The cohesive energy of the model nanowire systems was calculated by Quantum Sutton-Chen many body potential. The temperature and the pressure of the system were controlled by Nose-Hoover thermostat and Berendsen barostat, respectively. In addition effects of the diameter of nanowire on the mechanical properties were studied. The obtained results show that, when the diameter of Rh-20at%Pd nanowire increase, elastic constants, bulk modulus and Young modulus all increase, and when the diameter reaches about 5.5 nm, the properties began to level off and remain constant.**

Index Terms—**Mechanical properties, molecular dynamics simulation, Rh-20at%Pd nanowire.**

I. Introduction

The molecular dynamics simulation technique is a very powerful tool for studying of physical properties of materials in macro and nano scale. In this investigation, we used molecular dynamics simulation technique to study of Young modulus, bulk modulus as well as elastic constants of pure Rh and Pd metals as well as Rh-20at%Pd nanowire. Our simulation applied at constant temperature and pressure (NPT) ensemble. The quantum Sutton-Chen (Q-SC) potential [1]-[3] parameters of the pure Pd and Rh metals were used as interatomic potential parameters to calculate the cohesive energy as well as the mechanical properties of Pd and Rh pure metals and Rh-20at%Pd random alloys. We have calculated mechanical properties and cohesive energy of Pd, Rh elements under atmospheric pressure for evaluating computer codes and the interatomic potential.

The Pd-based alloys have been studied for more than 100 years with respect to both fundamental and applied aspects. Especially, in the last three decade thermodynamic and mechanical properties of pd-based alloys were studied by molecular dynamics simulation technique [1], [4], [5]. Among the Pd-based alloys, Rh-Pd alloy is of special interest owing to their increased hydrogen absorption capacity. Moreover, Pd based alloys can potentially offer improvements to pure Pd membranes. Very few experimental data are available for the mechanical properties of Rh-Pd nanowire; therefore calculation of thermal and mechanical properties of this nanowire is very important for industrial applications.

This paper is organized as follows. Section 2 details our simulation methodology that we use for equilibrium molecular dynamics simulation. In section 3, we present simulation results for the materials under investigation.

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II. Simulation Details

A. Interatomic Potential

In the present molecular dynamics simulation a Quantum Sutton-Chen [6] many body potential was employed, this potential give very good value for cohesive energy of Rh and Pd atoms [7], [8]. In this potential function, the cohesive energy of system obtain from following equation

$$U = \sum_i \left[\frac{1}{2} \sum_{j \neq i} \varepsilon V(r_{ij}) - c\varepsilon \sqrt{\rho_i} \right] \tag{1}$$

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

The first term, $V(r_{ij})$, describes the pairwise repulsive interaction between atoms i and j, and the second term, ρ_i, represents the many-body cohesive term associated with atom i. r_{ij} is the distance between atoms i and j , a is a length parameter scaling, c is a dimensionless parameter scaling, ε sets the overall energy scale, and n, m are integer parameters. The potential parameters of Rh, Pd and Rh-Pd are listed in Table I. To construct the potential for the binary alloy state, Rh-20%Pd, from the corresponding Q-SC potentials for the elemental state, we used the following mixing rule [7], [9]

$$m_{ij} = \frac{(m_i + m_j)}{2}, \; n_{ij} = \frac{(n_i + n_j)}{2}$$
$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}, \; a_{ij} = (a_i a_j)^{1/2} \tag{3}$$

TABLE I: The Q-SC Potential Parameter for RH-PD Model Alloy System

Interaction	$\varepsilon(eV)$	a(Å)	c	n	m
Rh-Rh	0.002461	3.7984	305.49	13	13
Pd-Pd	0.003286	3.8813	148.20	12	6
Rh-Pd	0.002843	3.8396	-------	12.5	9.5

B. Temperature and Pressure Control

The extended system method was used for temperature control. This method was originally introduced by Nose [10] and subsequently developed by Hoover [11], therefore this method was called Nose-Hoover thermostat. The introduction of this mechanism modifies the standard velocity Verlet equations of motion to the following form [12], [13]

$$\vec{r}_i(t+\delta t)=\vec{r}_i(t)+\delta t\vec{\mathrm{v}}_i(t)+\frac{1}{2}\delta t^2\left[\frac{\vec{f}_i(t)}{m_i}-\zeta(t)\vec{\mathrm{v}}_i(t)\right]$$
$$\zeta(t+\tfrac{1}{2}\delta t)=\zeta(t)+\frac{\delta t}{2Q}\left[\sum_i^N m_i\vec{\mathrm{v}}_i^2(t)-gk_bT\right]$$
$$\vec{\mathrm{v}}_i(t+\frac{1}{2}\delta t)=\vec{\mathrm{v}}_i(t)+\frac{\delta t}{2}\left[\frac{\vec{f}_i(t)}{m_i}-\zeta(t)\vec{\mathrm{v}}_i(t)\right] \quad (4)$$

$$\zeta(t+\delta t)=\zeta(t+\tfrac{1}{2}\delta t)+\frac{\delta t}{2Q}\left[\sum_i^N m_i\vec{\mathrm{v}}_i^2(t+\tfrac{1}{2}\delta t)-gk_bT\right]$$
$$\vec{\mathrm{v}}_i(t+\delta t)=\frac{2}{2+\delta t\zeta(t+\delta t)}\left[\vec{\mathrm{v}}_i(t+\tfrac{1}{2}\delta t)+\frac{1}{2}\delta t\frac{\vec{f}_i(t+\delta t)}{m_i}\right]$$

where ζ is the dynamic friction coefficient of the heat bath to which the system is coupled. This coefficient is not a constant and can take on both positive and negative values, leading to the deceleration or acceleration of the atoms respectively, if their total kinetic energy is greater, or smaller, than $gk_bT/2$. A particular parameterization of Q is given by

$$Q=gk_bT\tau^2 \quad (5)$$

where τ is the relaxation time of the thermostat. This parameter controls the speed with which the thermostat damps down the fluctuations in the temperature. The number of degrees of freedom, g, is given by $g=3(N-1)$.

The Berendsen barostat [14] was used to pressure control of system. This barostat uses a scale factor, μ, which is a function of instantaneous pressure, P, to scale lengths in the system.

$$\begin{aligned} x(i) &\to \mu x(i)\\ y(i) &\to \mu y(i)\\ z(i) &\to \mu z(i)\\ L &\to \mu L \end{aligned} \quad (6)$$

where μ is given by

$$\mu=\left[1-\frac{\delta t}{\tau_p}(P-P_0)\right]^{1/3} \quad (7)$$

Here, τ_p is the rise time of the barostat, and P_0 is the set point pressure. The system pressure is set toward a desired value by changing the dimensions of the simulation cell size during the simulation.

C. Mechanical Properties

The quantities which are calculated in this molecular dynamics simulation were the Young modulus, the elastic stiffness constants as well as the bulk modulus. According to the Hooke's law, for small deformation, the stress components σ_{ij} are directly proportional to the strain components ε_{ij}. This relation can be expressed in mathematical terms as

$$\sigma_{ij}=C_{ijkl}\varepsilon_{kl} \quad (8)$$

where C_{ijkl} are the elastic stiffness constants. The number of independent elastic stiffness constants is reduced if the crystal possesses symmetry elements. The elastic constants reduce to three constants, C_{11}, C_{12} and C_{44} for the cubic crystal by reason of symmetry [15]. In terms of interatomic potential, these quantities can be expressed as [16]

$$C_{11}=\frac{1}{\Omega}\frac{\partial^2U}{\partial\varepsilon_{11}^2}\ ,\ C_{12}=\frac{1}{\Omega}\frac{\partial^2U}{\partial\varepsilon_{11}\partial\varepsilon_{22}}\ ,\ C_{44}=\frac{1}{4\Omega}\frac{\partial^2U}{\partial\varepsilon_{12}^2} \quad (9)$$

where ε_{11}, ε_{12} and ε_{22} are the components of strain tensor, Ω is the volume, and U is the energy is given by Eq. 1, per atom.

The bulk modulus, which measure how the volume of the solid change with hydrostatic pressure, denoted by B. this is related to interatomic potential via [16]

$$B=\Omega\left(\frac{\partial^2U}{\partial\Omega^2}\right)_{\Omega=\Omega_0} \quad (10)$$

where Ω_0 is the equilibrium value of Ω.

We have used the Reuss assumption to estimate the Young modulus (E) according the following relations [17]

$$E=9GB/(3B+G) \quad (11)$$

where G is the shear modulus.

$$G=5(C_{11}-C_{12})/(4C_{44}+3(C_{11}-C_{12})) \quad (12)$$

D. Simulation Data

In this research, the molecular dynamics simulation is performed for different size of Rh-20at%Pd nanowire in NPT ensemble. We changed the diameter of nanowire and calculated mechanical properties, therefore size dependent of mechanical properties of nanowire were obtained. The simulation time step (δt) was set 0.05 fs for every run of MD simulation. The nanowire equilibrated during 10000 time steps in the T=100 K. Fig. 1 shows the variation of the energy of pure Rh, Pd and Rh-20at%Pd alloy in order to detect of the equilibrium state. Moreover variation of the pressure and volume are plotted in the Fig. 2. Both figures show fluctuation around constant value in the energy, pressure as well as volume. For translation from macroscale to nanoscale, the periodic boundary condition applied in the axis of nanowire only and removes at the other directions.

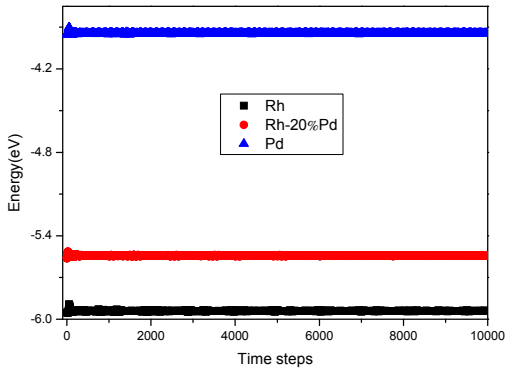

Fig. 1. Time variation of the energy for Rh, Rh-20at%Pd and Pd nanowires during equilibration.

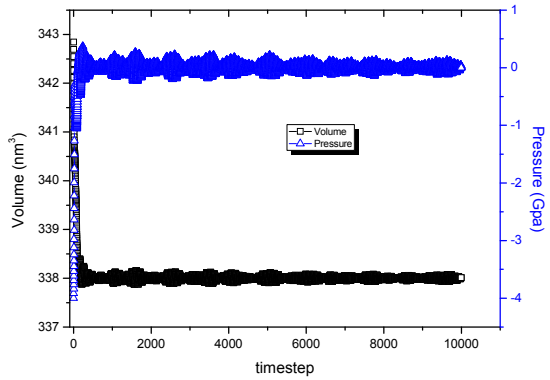

Fig. 2. Time variation of the volume and pressure for the Rh-20at%Pd nanowire during equilibration.

III. Results

At first, the cohesive energy, the elastic constants, the Bulk modulus and the Young modulus were calculated for pure Rh as well as Pd metals. Our motivation for computing these properties for the elemental materials was to obtain an estimate of the accuracy of the Q-SC potentials. A comparison of the results for the elemental materials shows that our computed values are in reasonable agreement with the experimental data that are available for these materials. This can give an indication of the quality of the alloy potential energy functions that we have constructed on the basis of these elemental potentials. The percentage errors associated with the computed values, as compared to the experimental data are listed in Table II.

The variations of the Young modulus, bulk modulus as well as elastic constants with Rh-20at%Pd nanowire diameter were computed in the MD simulation by changing the number of atoms in the nanowire (figures 3-7). Our computed results are in reasonable agreement with other results in the literature where they are available. From these figures we see that there is an initial change in the mechanical properties with the diameter of the nanowire, following which the properties remain unchanged as the nanowire grows in diameter. This is a typical behavior of nanoscopic system in which the mechanical properties, for example, change with size, and then reach a constant value. These results show that, when the diameter of nanowire increase, C_{11}, C_{12}, C_{44} , bulk modulus and Young modulus all increase, and when the diameter reaches about 5.5 nm, the properties began to level off and remain constant.

TABLE II: The Percentage Error of the Computed Values VIS-À-VIS the Experimental Data

Physical properties	Pd	Rh
U	0.2	0.8
C_{11}	2.6	3.2
C_{12}	16.2	5.7
C_{44}	44.3	17.5
B	15.7	9.5
E	5.3	11.5

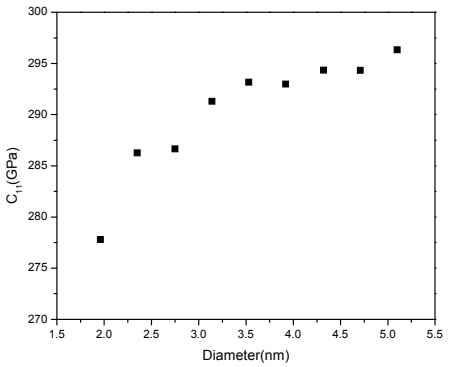

Fig. 3. Variation of elastic constant (C_{11}) of Rh-20at%Pd nanowire with diameter of nanowire.

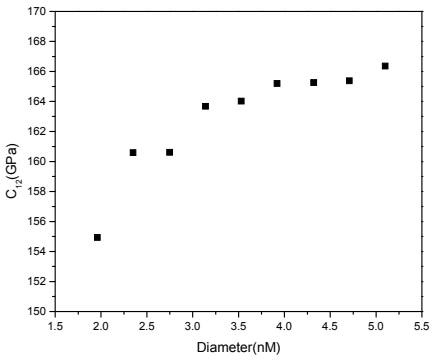

Fig. 4. Variation of elastic constant (C_{12}) of Rh-20at%Pd nanowire with diameter of nanowire.

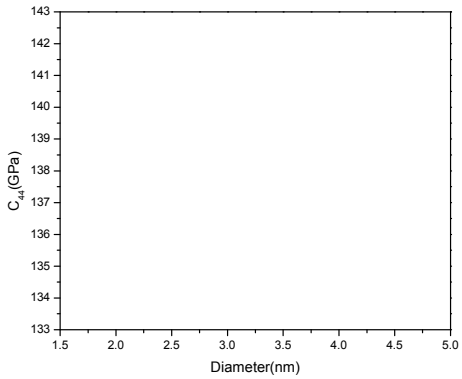

Fig. 5. Variation of elastic constant (C_{44}) of Rh-20at%Pd nanowire with diameter of nanowire.

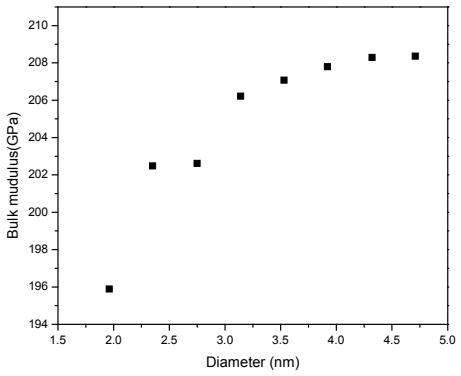

Fig. 6. Variation of bulk modulus of Rh-20at%Pd nanowire with diameter of nanowire.

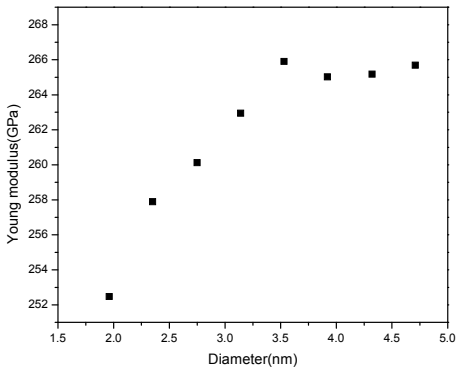

Fig. 7. Variation of Young modulus of Rh-20at%Pd nanowire with diameter of nanowire.

In summary, the results of molecular dynamics simulation of pure Rh and Pd metals show that our simulation results are in reasonable agreement with the experimental data. Moreover, Our MD results of Rh-20at%Pd nanowire show that, the mechanical properties depend on the diameter of the nanowire and the values of elastic constants, Young modulus and bulk modulus of the nanowire are different from the properties of the bulk alloy.

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