THE EFFECT OF THE COOLING RATE ON THE SOLIDIFICATION OF THE LIQUID Pd NANOPARTICLE

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Abstract

In this work, we have investigated the effect of the cooling rate on the solidification behavior of liquid Palladium (Pd) nanoparticle by using molecular dynamics simulation. We considered the following properties in detail: the temperature dependence of the total energy and the pair distribution functions. The Wendt-Abraham parameter was calculated to determine the crystallization and glass transition temperatures of Pd nanoparticle. The results showed that the solidification behavior of the nanoparticle differs as the cooling rate changes.

Keywords: Pd nanoparticle, MD simulation, solidification, glass transition temperature.

INTRODUCTION

Metal nanoparticles having a size of less than 10 nm in recent years have attracted a great deal of attention of researchers, because of their physical, chemical and electronic properties differ greatly than that of bulk material. For example, Pd nanoparticles are widely used in heterogeneous catalysis because of their ability to facilitate catalytic reactions and to obtain high surface energy metals [1,2].

As metal nanoparticles are generally produced with high heat treatments such as evaporation and aerosol methods, it is important to investigate their structural evolutions during solidification or condensation [3,4]. Atomic simulation techniques, such as molecular dynamics (MD), play an important role in explaining the structural properties of the system during the solidification of the nanoparticles, as they have the ability to analyze more than experimental studies. For example, MD simulations allow to observe glass transition at high cooling rates which cannot be reached in experiments. In the literature, there are many studies investigating the effect of cooling rate on the solidification process of liquid metal nanoparticles using the MD simulation method [5-7].

In present work, we have investigated effects of the cooling rate on the solidification process of liquid Pd nanoparticle by using MD simulation with the quantum Sutton – Chen (QSC) potential [8,9].

EXPOSITION

One of the most important factors affecting the accuracy of MD simulations is the interatomic potential that define the interactions between atoms in the system. Therefore, when selecting interatomic potential to be used in MD simulations, this potential should be tested whether the interactions between the atoms in the system are correct. In this study, QSC potential was used for interactions between Pd atoms. This potential was previously tested correctly by Cagin et al. [9] for bulk Pd. In the QSC model, the total potential energy is expressed as follows [9]:

$$U_{tot} = \sum_i U_i \,, \tag{1}$$

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

where $V(r_{ij})$ is a pair potential between atoms i and j separated by the distance of r_{ij} to account for the repulsion resulting from Pauli's exclusion principle and ρ_i is a energy density term accounting for cohesion associated with atom i.

$$V(r_{ij}) = \left(\frac{a}{r_{ij}}\right)^n, \quad (3)$$

$$\rho_i = \sum_{j \neq i} \varphi(r_{ij}) = \sum_{j \neq i} \left(\frac{a}{r_{ij}}\right)^m. \quad (4)$$

where the a is a parameter with the dimension of length leading to dimensionless $V(r_{ij})$ and ρ_i, c is a dimensionless parameter, ε is a parameter with the dimension of energy, and n and m are positive integers providing that $n > m$. We use the QSC potential which its parameters are listed in Table 1, to describe interatomic interactions.

Table 1. *QSC potential parameters for Pd* [9]

Metal	ε (eV)	c	a (Å)	n	m
Rh	3.2864×10^{-3}	148.205	3.8813	12	6

In this study, MD simulations were performed for approximately 5 nm diameter (4508 atom) Pd nanoparticle using the DLPOLY code [10]. The nanoparticle was extracted from a large crystal structure of the ideal *fcc* Pd using a series of spherical cutoffs. MD simulations were carried out under constant volume and constant temperature NVT ensemble without the periodic boundary conditions. The Newtonian equations of motion are integrated using the Leapfrog Verlet method with a time step of 1fs. The desired temperature and ambient pressure are controlled by Nose- Hoover thermostat and Berendsen approach, respectively. The solidification temperature (T_c) and glass transition temperature (T_g) are obtained as follows: first, the nanoparticle is heated from 50K with an increase of ΔT = 50 K until it is completely melt. During heating, the simulations is performed for 100 ps equalization, followed by a 50 ps production time to produce time averaged features at each temperature. Once the nanoparticle has been melted, it is equilibrated with a constant temperature and constant volume (NVT) ensemble with 250000 MD steps at T = 1800K. Then, the system is cooled from this temperature to a temperature of 50K with cooling rates of γ = 0.05 K/ps, γ = 0.5 K/ps, γ = 5 K/ps and γ = 50 K/ps, in order to investigate the effect of the cooling rates on the solidification behavior.

The phase transition temperature of the Pd nanoparticles from the solid phase to the liquid phase or from the liquid phase to the solid phase can be readily identified from the sudden increase in total energy. Figure 1 shows the change of the total energy curves per atom of the Pd nanoparticle with the temperature during the heating and cooling.

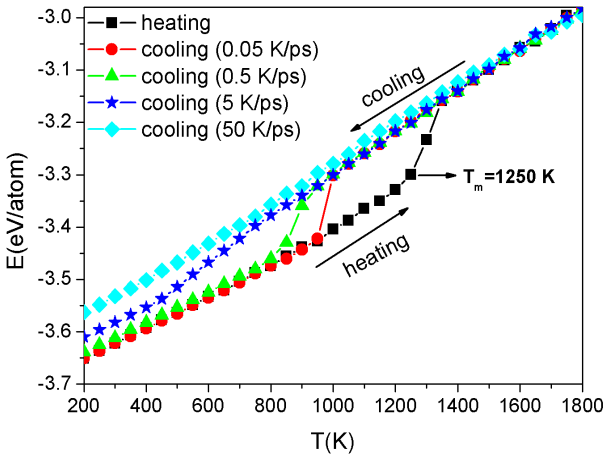

Fig. 1. *Temperature dependence of the total energy of Pd nanoparticle during the heating and cooling processes*

From the heating curve, it is observed that the energy curve is linearly related to the temperature before the melting point (T_m). The energy curve showed a sudden increase at T_m = 1250 K and the system transforms from solid phase to liquid phase. The nanoparticle continues a linear increase in energy with temperature in the liquid phase. From the cooling curve, the energy of the liquid Pd nanoparticle at all cooling rate varies similarly, regardless of the cooling rate, down to about 1050K. Although there is a sudden decrease in energy in cooling rates of γ = 0.05 K/ps, γ = 0.5 K/ps, γ = 5 K/ps, there is no sudden decrease in γ = 50 K/ps cooling rate. For γ = 0.05 K/ps, γ = 0.5 K/ps, γ = 5 K/ps cooling rates, the temperatures at which this sudden decrease in energy occurs are 950K, 850K, 700K, respectively. This change in energy indicates that for γ = 0.05 K/ps, γ = 0.5 K/ps, γ = 5 K/ps the liquid Pd nanoparticle is transformed to the solid phase at these temperatures. One of the best ways to observe the phase transition of a system is to analyze the characteristic behavior of the pair

distribution function (PDF) with temperature. PDF is defined as [11]:

$$g(r) = \frac{\Omega}{N^2}\langle(\sum_{i=1}^{N_i} n_i)/4\pi r^2\Delta r\rangle \qquad (5)$$

where, $g(r)$ is the probability of finding an atom in a distance ranging from r to $r+\Delta r$. Ω is simulated volume of unit cell. N is the number of atoms in the systems, and N_i is the averaged number atom around ith atoms sphere shell ranging r to $r+\Delta r$, where Δr is the step of calculation.

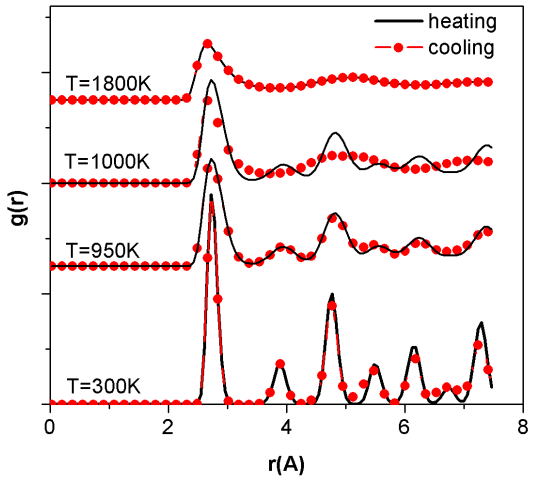

Fig. 2. *PDFs of Pd nanoparticle during heating and cooling (γ =0.05K/ps) at different temperatures*

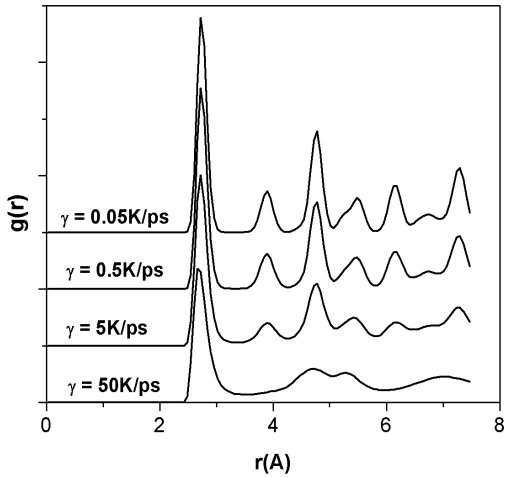

Fig. 3. *PDFs of the liquid Pd nanoparticle cooled with different cooling rates at 300 K*

The PDFs of Pd nanoparticle calculated at different temperatures during heating and cooling processes at the rate of γ = 0.05 K/ps are given in Figure 2. The PDFs obtained from both heating and cooling processes overlap at 1800K. When the Pd nanoparticle is cooled to 1000 K, it is seen that the system still remains in the liquid phase known as the supercooled region, whereas the nanoparticle is in the solid phase during the heating process for the same temperature. The characteristic behavior of the PDFs obtained at 950 K and 300 K during both the heating and cooling process shows solid phase characteristics. Pd nanoparticle transform from liquid phase to solid phase at 950K during cooling process. Figure 3 shows the PDFs of the Pd nanoparticle obtained by cooling with different cooling rates at 300K. As can be seen from Figure 3, it is clear that the Pd nanoparticle is in the solid phase from the characteristic behavior of the PDFs at 300K for cooling rates of γ = 0.05 K/ps, γ = 0.5 K/ps and γ = 5 K/ps. However, it can be said that the nanoparticle is in the amorphous phase of the characteristic behavior of the PDF for the cooling rate of γ = 50 K/ps at 300K. For the 50 K/ps cooling rate, a splitting occurs in the second peak of the PDF. This splitting, which is seen at the second peak of the PDF, is one of the most important indicators of the transition of the system from the liquid structure to the glassy structure.

In this study, we used the Wendt-Abraham (WA) parameter to obtain the T_c and T_g temperature more precisely. It is defined as $R^{WA} = g_{min}/g_{max}$, in which g_{min} and g_{max} are the first minimum and maximum values of PDF curve, respectively [12]. The R^{WA} parameters calculated for four different cooling rates are given in Figure 4 as a function of temperature.

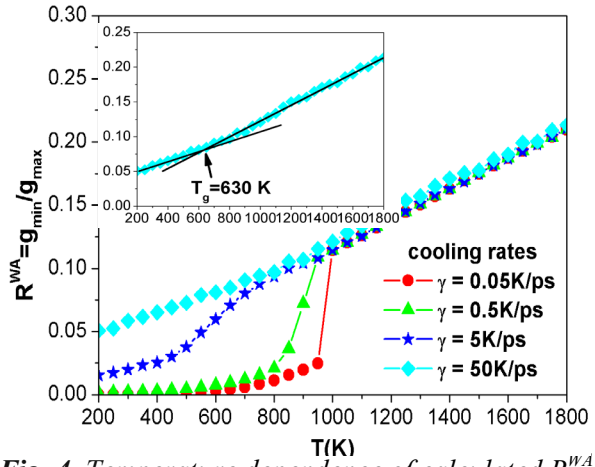

Fig. 4. *Temperature dependence of calculated R^{WA} values at different cooling rates for Pd nanoparticle*

In the cooling process, as seen from the change of the WA parameter with temperature, there is a sudden decrease in the WA values of γ = 0.05 K/ps, γ = 0.5 K/ps and γ = 5 K/ps cooling rates at 950K, 850 K and 700K, respectively. This sudden decrease indicates that the Pd nanoparticle has transformed from the liquid phase to the crystalline phase. However, there is no such decrease in the WA

parameter for γ = 50 K/ps cooling rate. The WA parameter for γ = 50 K/ps cooling rate exhibits a linear relation with temperature. This linear relation observed in the WA parameter for γ = 50 K/ps cooling rate is an indication that the system has transformed from a liquid structure to a glassy-like structure. The value of T_g is obtained from the intersection point of the linear fit curves (see Fig. 4). These results, obtained from the change of the WA parameter with temperature for the Pd nanoparticle, previously support the above analyzes. T_c and T_g temperatures obtained from the results of all these analyzes for the liquid Pd nanoparticle are listed in Table 2.

Table 2. *T_c and T_g temperatures for liquid Pd nanoparticle.*

Cooling rates	T_c (K)	T_g (K)
γ = 0.05 K/ps	950	---
γ = 0.5 K/ps	850	---
γ = 5 K/ps	700	---
γ = 50 K/ps	---	630

As can be seen from the data in Table 2, as the cooling rate decreases, the temperature value at which the system starts to crystallization is increased. In addition, the transformation of the system from liquid structure to crystalline structure or glassy structure depends directly on the cooling rate.

CONCLUSION

We have investigated the effect of the cooling rate on the solidification behavior of liquid Pd nanoparticle with 5nm (4508 atoms) diameter by using molecular dynamics simulation with QSC potential. The results from the MD simulations explain that there is a direct relationship between the solidification behavior of the liquid Pd nanoparticle and the cooling rate. The more time we spend for cooling the system, the higher temperature it starts to crystallize. If we cool the system too fast, the system prefers to transform into a glassy structure.

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