THE STUDY OF MOLECULAR DYNAMICS SIMULATIONS OF MELTING BEHAVIOR OF BCC TANTALUM NANOCLUSTERS

Murat CELTEK[1], Unal DOMEKELI[2]
[1]*Faculty of Education, Trakya University, Edirne, Turkey*
[2]*Faculty of Science, Trakya University, Edirne, Turkey*

Abstract
Tantalum (Ta) is used in a wide variety of technological fields such as production of high-temperature superalloys, microelectronics and nuclear power, because of its high melting temperature and strength. It is known that nanoparticles can exhibit unusual chemical and physical properties from those of the bulk metals. In this work, molecular dynamics simulations were performed to investigate the thermal properties of unsupported metallic Ta nanoparticles. The size dependent structural properties of Ta nanoparticles were analyzed by caloric curves and radial distribution functions. We observed that the melting temperatures of Ta nanoparticles is lower than that of bulk Ta, and it decreases with reducing diameter in nanoscale regime.

Keywords: Tantalum, Classical molecular dynamics simulations, Melting of nanoparticle, Pair distribution functions.

INTRODUCTION

Nanomaterials have a great attraction from researches because of having different physical and chemical properties from their bulk counterparts because of structural characteristics and size effects [1]. Due to high surface to volume ratio, the decreasing of the melting temperature of a metallic system is one of the important results of the reduction of size of that system. Some thermodynamic approximations have been made to give a predictions on decreasing melting temperature. As we know, a general theoretical model that predicts the melting mechanism for all nano-systems has not been developed, yet. Molecular dynamics simulations (MD) are effective solution to observe time evolution of any system. They are used to give detailed information on melting process such as melting of clusters having higher melting point than bulk material [2], premelting behavior [3], dynamic coexistence states near melting [4].

Tantalum (Ta), which is body-centered-cubic (bcc) transition metal with no confirmed experimentally observed solid-solid phase changes with pressure or temperature, is used in a wide variety of applications ranging from microelectronics to nuclear power because of its high melting temperature and strength [5]. For example, to increase the quality and reduce the size of the packaging, researchers need thin and flexible Ta powders. So nano Ta has a wide range of applications[6].

In this work, we mainly focused on the thermal properties of Ta nanoparticles (NP). MD simulations with embedded atom method potentials (EAM) proposed by Daw and Baskes [7] were performed to observe melting process and size dependent structural properties which analyzed by caloric curves and radial distribution functions.

EXPOSITION

The EAM potential describing the energetics of pure and multicomponent metallic systems, accurately predicts physical and thermodynamic properties of them such as the melting temperature, phase transition, liquid density and local atomic environment [8]. The total energy of the metals is written as:

$$E_{tot} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{j \neq i} \phi(r) \quad (1)$$

where r is the distance between atoms, and $\phi(r)$, $\rho(r)$, and F are the pair, density, and embedded functions, respectively [7]. More details on the validation of the developed

EAM potential for metallic systems can be found elsewhere...

All simulations in this work were performed by using large-scale atomic/ molecular massively parallel simulator (LAMMPS) package [9]. To define the interactions between Ta atoms in simulation box, we used the EAM potentials parameterized with the force-matching method based on ab initio molecular dynamics by Sheng et al.[10]. The developed EAM potentials can be found in a tabulated form at https://sites.google.com/site/ eampotentials/Ta.

For the case of simulation of bulk material, MD simulation box was ideal bcc lattice with 6750 atoms. Periodic boundary conditions were applied for all directions. The timestep was 1fs. The system was equilibrated for 0.5 ns and subjected to continuous heating process from 300 K to 4200K for 6 ns within the restrictions of the constant pressure-temperature-number of atoms (NPT) ensemble. The nanoparticles were extracted from the large perfect bcc supercell with the eight different diameters. Prepared initial nano-systems were annealed at room temperature to obtain stable structure for 1 ns using constant volume-temperature (NVT) ensemble. Then, they gradually heated with the heating rate of $5.3 \cdot 10^9$ K/s up to 3500 K, which is higher than the melting point of bulk Ta.

First, we tested the EAM potential by calculating some ground state properties such as lattice parameter, cohesive energy elastic constants and melting point of bulk Ta. Table 1 lists simulated solid state properties of bulk Ta along with the experimental data. The solid state properties are in good agreement with literature. We should note that we have used two-phase simulation scheme to obtain melting point because the continuous heating yields overheated bcc Ta. In this context, the half of the simulation box was initially bcc solid state and another half liquid. MD simulations were performed in the constant pressure-enthalpy-number of particle (NPH) ensemble. Entire system was equilibrated at a certain temperature for a 4 ns. If the equilibrium temperature of the simulation is too low, the solid volume will begin to melt. We can determine the melting point whether below or above the melting temperature of real system by observing the moving of solid-liquid interface line. The determined melting temperature within this method was 3290 K (±20K) which is in very good agreement with experimental value.

Table 1. *Ground state properties of buk Ta*

property	*EAM*	*Expt.*
a_o(A) (300 K)	3.298	3.306[1]
E_c(eV/atom) (0 K)	-8.10	-8.10[1]
C_{11} (GPa)	283	261[2]
C_{12} (GPa)	169	157[2]
C_{44} (GPa)	95	82[2]
T_m (K)	3290	3290[3]

[1]http://www.webelements.com/tantalum/crystal_structure.html
[2]Ref.[11]
[3]Ref.[12]

Figure 1 plots the pair distribution functions (PDF) for solid and liquid bulk Ta along with the available other theoretical result of Jakse et al. [13]. Inset shows a comparison of the static structure factor obtained by Fourrier transform of PDF with experimental [5]. For the solid state, PDF has sharp and narrow peaks reflecting long range crystalline bcc lattice. An agreement in terms of peak position between simulated and other theoretical result is fair, except for amplitude of oscillations. From the results listed in Table 1 and PDF at low and high temperatures, we conclude that EAM potentials used in here successfully produce solid state properties of Ta and can be transferred to high temperatures to study liquid state of Ta NPs.

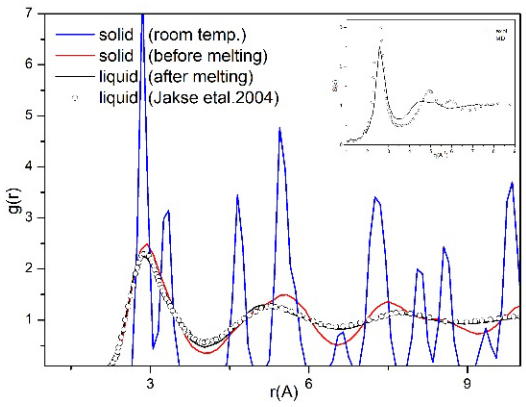

Fig. 1. *Pair distribution functions for solid and liquid bulk Ta. The inset plots static structure factor from MD with experimental data*

Figure 2 displays the temperature dependence of potential energy for Ta NPs with the comparison of the simulation results for continuous (direct) heating of bulk Ta. The potential energies of NPs which has large surface to volume ratio, is much higher than that of bulk. A sharp increasing in the potential energy was observed at the temperature of first – order phase transition during heating both NPs and bulk. As we mentioned above, this temperature is very high with respect to experimental melting point of bulk material because the continuous heating leads to overheating. The height of the sharp increasing is a measure of heat required for melting, and it increases as the size of nanoparticle increases. The melting temperatures, which are the midpoints of the sharp increase, obtained by present MD simulations of Ta NPs are listed in Table 2. The melting point of NP increases with increasing the size of NP, which reveal that the thermal stability of small nanoparticles must be carefully investigated before they can be used in applications such as nano-devices [14].

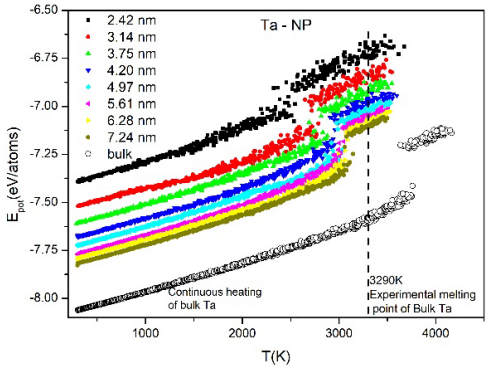

Fig. 2. *Potential energy as a function of temperature for bulk and Ta NPs*

Table 2. *The diameter, number of atoms and melting points of Ta NPs in present simulations*

D (nm)	*N (atoms)*	*T_m (K)*
2.42	531	2520±20K
3.14	1037	2660±20K
3.75	1810	2860±20K
4.20	2864	2930±10K
4.97	4285	2970±10K
5.62	6161	3055±10K
6.27	8393	3065±10K
7.22	11182	3070±10K
Bulk*	6750	3710±10K
Bulk**	48000	3290±10K

*The result for continuous heating simulation.
**The result for two-phase melting simulation.

We have calculated the melting points of ta NPs by using the theoretical model for nanosolids developed by Li et al.[15]. The size dependence of melting point of NP is plotted in Figure 3 with the theoretical model of Li et al [15]. It is clear that the melting points of the NPs decrease non-linearly with inverse size, the melting point predicted by the theoretical model reaches the experimental value of the melting limit for the bulk Ta at around 3300 K.

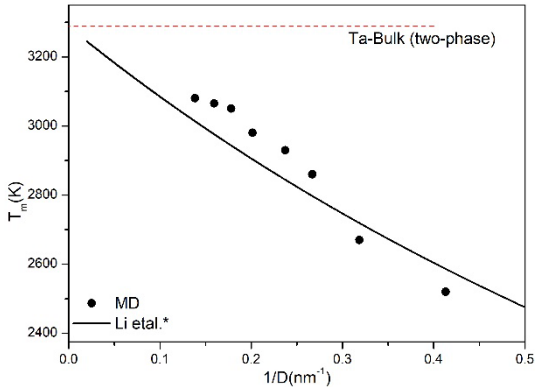

Fig. 3. *Simulated melting temperature versus invers diameter with the results of theoretical model of Li et al. [15]*

CONCLUSION

We have investigated the size effect on melting of Ta nanoparticles with spherical shape by the MD simulations in which interactions defined by means of EAM potential. We observed that melting temperatures of Ta NPs are lower than those of bulk Ta and decrease with the reducing diameter, in nanoscale regime. We conclude that the EAM Potential parameterized by Sheng et al [10] is successfully used for understanding the liquid structure of Ta and the size dependent thermodynamic properties of spherical Ta NPs.

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