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The stability of the β-phase of tantalum: a molecular dynamics study

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Abstract

Molecular dynamics simulations have been performed on tantalum clusters using the embedded-atom-method potential. Melting simulations show that β-Ta clusters have a lower melting temperature than the same size clusters of α-Ta (bcc structure). Pure β-Ta clusters are quite stable and do not transform to the α-Ta on melting. Simulations on Ta clusters with mixed α- and β-phases reveal that inclusion of a bcc-Ta cluster within a β-Ta cluster induces the β-to-α-phase transformation at a temperature far below the melting point of a pure β-Ta cluster, depending on the cluster size and α-to-β-atom ratio. The results suggest that the observed phase transformation of β-Ta thin films is due to the presence of α-phase inclusions in the β-Ta film grains.

1. Introduction

Ta films are very useful in the microelectronics industry, especially as an underlayer material in computer integrated circuits [1, 2]. Tantalum thin films exhibit two crystalline phases, bcc (α-phase, the bulk structure of tantalum) and a metastable tetragonal β-phase. The latter phase has been found to transform to the α-phase upon heating to ∼800–1000 K [3–5]. The structure of deposited thin films is usually the metastable β-phase or a mixture of two phases. Special attention has been paid to β-tantalum because the mechanisms stabilizing the β-phase are not well understood.

In our previous work [6], we showed that β-Ta forms on a broad range of substrates and under varying deposition conditions. Molecular dynamics simulations revealed that clusters of β-phase are quite stable at room temperature in contrast to fcc cuboctahedrons, icosahedrons and ball-cut hcp clusters which are not stable and quickly transform to bcc structure at room temperature. In addition, our preliminary computations suggested that the β-phase may be stable at temperatures much higher than indicated by experiments.

In order to understand the stability of the β-phase and the origin of the β-to-α-phase transformation, we further investigate the melting of α-phase and β-phase tantalum clusters. The trends for melting temperature versus cluster size were obtained for both β-phase and

α-phase. β-to-α-phase transformation was not observed for pure β-phase clusters before melting. However, deposited β-phase tantalum films were often observed to transform to the bcc structure at temperatures ∼800–1000 K [3–5]. A systematic study on the tantalum clusters with mixed phases revealed that inclusion of an α-phase cluster within a β-Ta host cluster enables the β-to-α transformation. This study provides insight into the often reported [3–5] β-to-α-phase transformation found with β-Ta thin films.

2. Computational detail

2.1. Molecular dynamics

Molecular dynamics was performed using the IMD code originally developed by Stadler [7, 8]. Tantalum clusters were modelled using an embedded-atom-method potential and the force-matching method [9, 10]. Simulations were conducted in the canonical ensemble at a constant temperature. The time step was chosen as 3.5 fs throughout all simulations. Typically runs require approximately 0.35 ns (1×10^5 time steps), and sometimes twice as long (0.70 ns) when necessary, e.g. near the transition temperature in melting or α-to-β-phase change. The radial distribution functions (RDFs) were obtained from the end structure as the average over 100 time steps after the cluster was brought to thermal equilibrium.

The EAM potential developed by Li *et al* [10] has been fitted to a variety of experimental data (elastic constants, lattice constant, cohesive energy and unrelaxed vacancy formation energy) and density-functional theory (DFT) force data for a number of structures including clusters, surfaces, interstitials, vacancies, liquids, and stacking faults. This potential can be applied to calculating equilibrium as well as nonequilibrium properties for Ta. Compared with other empirical potentials previously proposed in the literature [11–15], the EAM potential is a preferred approach for describing the properties of Ta clusters and the β-Ta phase. Thus, in spite of the quantitative limitations of EAM, we expect the potential to produce a qualitatively correct description of the nanoclusters.

2.2. Melting of α-Ta and β-Ta clusters

Two groups of Ta clusters were constructed based on two phases (α and β) formed in deposited tantalum thin films, which are called α-Ta clusters and β-Ta clusters. α-Ta clusters are rhombic dodecahedrons cut from the bcc lattice with surfaces along [110] planes. They are shelled structures [16, 17]. Packing of atoms to produce a given polyhedral form leads to sequences of atom numbers in clusters with complete outer shells, which are called magic numbers [16, 17]. Rhombic dodecahedrons (bcc) have a size sequence of 175, 369, 671, 1105, 1695, 2465, 3439, 4641. β-Ta clusters have ball shapes cut as a sphere from the σ structure of β-Ta phase with the $P\bar{4}2_1m$ space group [9, 10]. They have incomplete outer shells with the size sequence of 129, 505, 1325, 1823, 2761, 3561, 5005. Their initial atomic positions are taken to be those of bcc and tetragonal tantalum lattices with lattice constants $a = 0.331$ nm and $a = 1.0211/c = 0.530\,64$ nm, respectively.

We have performed a general investigation of melting of two group clusters. The caloric curves were obtained using a sequence of constant temperature simulations. The temperature steps were changed in a range of 10–200 K, depending on the 'distance' from the transition, which would be anticipated from the behaviour of the potential energy. A small temperature step of 10 K is used upon approaching the transition.

2.3. Phase transformation of mixed-phase tantalum clusters

For the phase transformation investigation, tantalum clusters with mixed phases were constructed. Ball clusters were comprised of a sphere of α-Ta at the centre and a β-Ta shell.

Table 1. Phase transformation of three mixed-phase cluster groups related to the temperatures and their α to β atom ratios. (N, no phase transformation; Y, phase transformation; ∼Y, very slow phase transformation.)

Groups	Total atom no.	α-Ta atom no.	α to β atom ratio	Temperature (K) 1000	1500	2000
3000-atom group	2 989	259	0.094 87	N	N	N
	2 987	331	0.124 6	N	N	N
	2 971	411	0.160 6	N	N	Y
	2 985	459	0.181 7	N	Y	Y
	2 983	531	0.217 6	Y	Y	Y
	2 977	609	0.257 2	Y	Y	Y
	2 965	749	0.338 0	Y	Y	Y
6500-atom group	6 519	411	0.067 29	N	N	N
	6 509	459	0.075 87	N	N	N
	6 511	531	0.088 80	N	N	Y
	6 519	609	0.103 1	N	N	Y
	6 519	749	0.129 8	N	∼Y	Y
	6 513	941	0.168 9	∼Y	Y	Y
	6 521	1037	0.189 1	Y	Y	Y
	6 529	1139	0.211 3	Y	Y	Y
10 000-atom group	10 045	609	0.064 54	N	N	N
	10 069	749	0.080 37	N	N	N
	10 069	821	0.088 78	N	N	Y
	10 063	941	0.103 2	N	N	Y
	10 011	1037	0.115 6	N	N	Y
	10 045	1139	0.127 9	N	∼Y	Y
	10 037	1363	0.157 1	∼Y	Y	Y
	10 003	1591	0.189 1	∼Y	Y	Y
	10 027	1837	0.224 3	Y	Y	Y

They were constructed in the following way: first build a sphere of a β-Ta cluster with radius r_1 as previously described, with one Ta1 (A) (notation of [18]) at the centre, having (0, 0, 0) coordinates; then replace all tantalum atoms which are located within a centred sphere with radius r_2 much less than r_1 with atoms from a sphere of an α-Ta cluster cut from bulk bcc tantalum. Their atomic positions are taken from bcc and tetragonal tantalum lattices with their respective unit cell vectors a, b, c, accordingly parallel to the x, y, z axes of the same coordinate system. Thus the cluster has two phases with the α-Ta sphere incorporated in a β-Ta shell with a spacing of ∼0.286 nm between the external surface of the α-Ta sphere and the internal surface of the β-Ta cluster. The atom distribution at the interface will slightly change, depending on the r_2 value. This approach is used as a model system to understand the β-to-α-phase transformation. Tantalum thin films with mixed phases may have small α-Ta grains surrounded by other β-Ta grains with grain boundaries between them. Weak α-Ta peaks have been seen in x-ray diffraction patterns of β-Ta films [6, 19, 20]. Ta clusters were divided into three groups according to the total numbers of atoms, approximately 3000, 6500 and 10 000 atoms. Each group has a combination of clusters with different α to β ratios. The details of cluster group can be found in table 1.

The simulations were carried out for each group in the microcanonical ensemble at three temperatures, 1000, 1500 and 2000 K. The phase transition was determined on the basis of the behaviour of the potential energy. A large potential energy decrease indicates phase change.

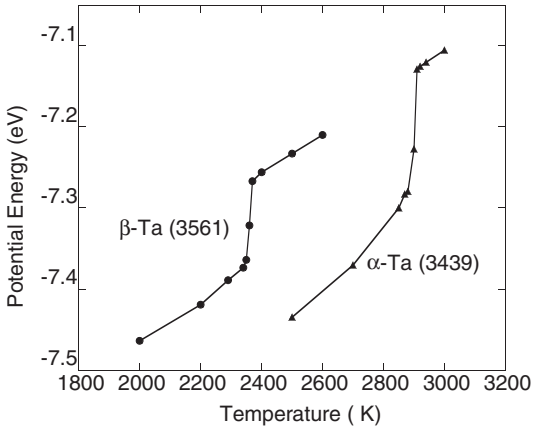

Figure 1. Caloric melting curves for 3561-atom α-Ta cluster and 3439-atom β-Ta cluster.

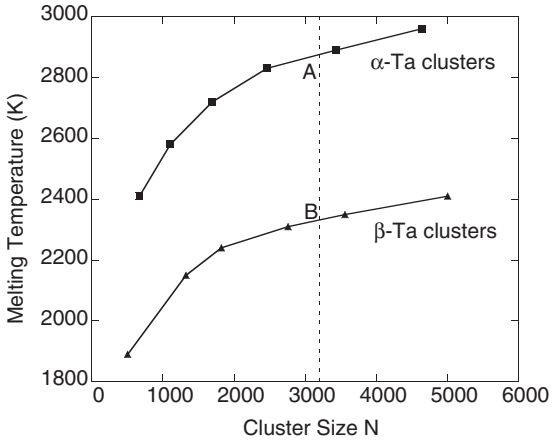

Figure 2. Melting temperature as a function of cluster size for α-Ta and β-Ta clusters.

The radial distribution functions (RDFs) of end structures were also used to check if the transition occurs.

3. Results

3.1. Melting temperatures

The caloric melting curves were obtained for each cluster of α-Ta and β-Ta groups as shown for the 3439-atom α-Ta cluster and the 3561-atom β-Ta cluster in figure 1. The potential energy varies smoothly, almost linearly with temperature on either side of the melting points, where a large jump in energy occurs. Very near the transition, the system becomes unstable; the fluctuating energy points are characteristic of a transient state. Note that 'hysteresis' in the melting point sometimes occurs in MD simulations [21, 22]. The melting temperature can be higher than the thermodynamic transition point. For all β-Ta clusters no β-to-α-phase change was observed, even near the melting temperature, which suggests the stability of β-Ta clusters as discussed in our previous work [6].

The melting temperature was plotted as a function of cluster size for α-Ta and β-Ta cluster groups in figure 2. The melting points show a general increase with cluster size as expected.

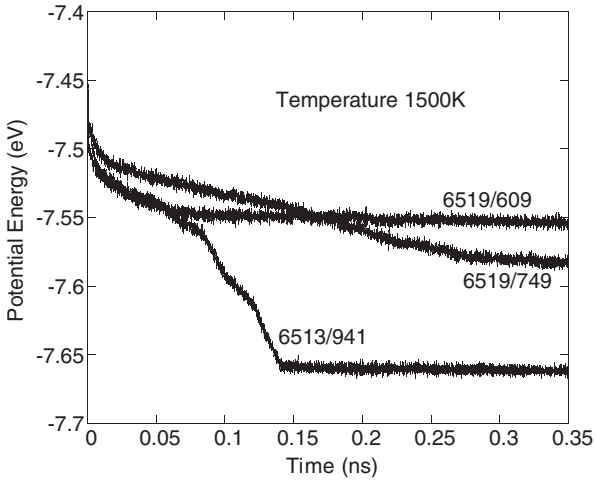

Figure 3. Potential energy (per atom) as a function of time for clusters with mixed α- and β-phases in 6500-atom group at 1500 K.

All melting points of α-Ta clusters lie below the bulk bcc melting point 2996 K [23] due to the small cluster size, but the expected basic trends are reproduced. The melting temperature for bulk β-Ta is unknown. In deposition experiments, β-Ta thin films were observed to transform to α-phase at the temperature $\sim$800–1000 K before melting. In our simulation, the β-Ta clusters were not observed to undergo phase change before melting. The melting curve of β-Ta clusters (figure 2) shows that the melting point of bulk β-Ta may be located around 2500 K, which is much lower than bulk bcc tantalum. Analysis of the two melting curves suggests a Ta cluster, which melts at temperature A if it is β-phase and melts at B if bcc phase, can have two possible states between temperature A and B, undercooled liquid or stable bcc solid. This can be explained by the hysteresis expected in the melting/freezing transition. The melted β-Ta clusters can be considered undercooled liquid before recrystallizing.

3.2. Phase transformation of Ta clusters with mixed phases

The energies were plotted as a function of simulation time in figure 3 as represented by the evolution of clusters in the 6500-atom group at 1500 K. All clusters show a decrease in energy at the beginning of a simulation because of the structural relaxation from the starting configurations. Subsequently, the 6513/941 cluster (a mixed-phase cluster having a total of 6513 atoms with 941 α-Ta atoms) shows a steep energy drop between 0.1 and 0.15 ns, while the 6519/609 cluster is stable after the initial relaxation. The RDF of initial and end structures of 6513/609 and 6513/941 clusters (figure 4) are compared with those of the pure bcc 6095-atom cluster (a rhombic dodecahedron) and a 6493-atom ball β-phase cluster relaxed at 1500 K. The 6513/941 cluster ends with almost the same RDF as the 6095-atom bcc cluster, indicating that a phase change from β to α occurred. The large decrease in energy seen in figure 3 is due to the phase change. However, the 6519/609 cluster, which has a lower α to β atom ratio than the 6513/941 cluster, maintains the RDF feature of β-Ta clusters as compared to the relaxed 6493-atom β-Ta cluster. Analysis of RDF and energy behaviour for all clusters in the 6500-atom group shows rapid transformation in clusters with α-to-β ratio equal to or larger than 0.1689 (6513/941) but not in clusters with ratio equal to or less than 0.1031 (6519/609). The 6519/749 cluster with an in-between atom ratio experiences very slow phase change, as

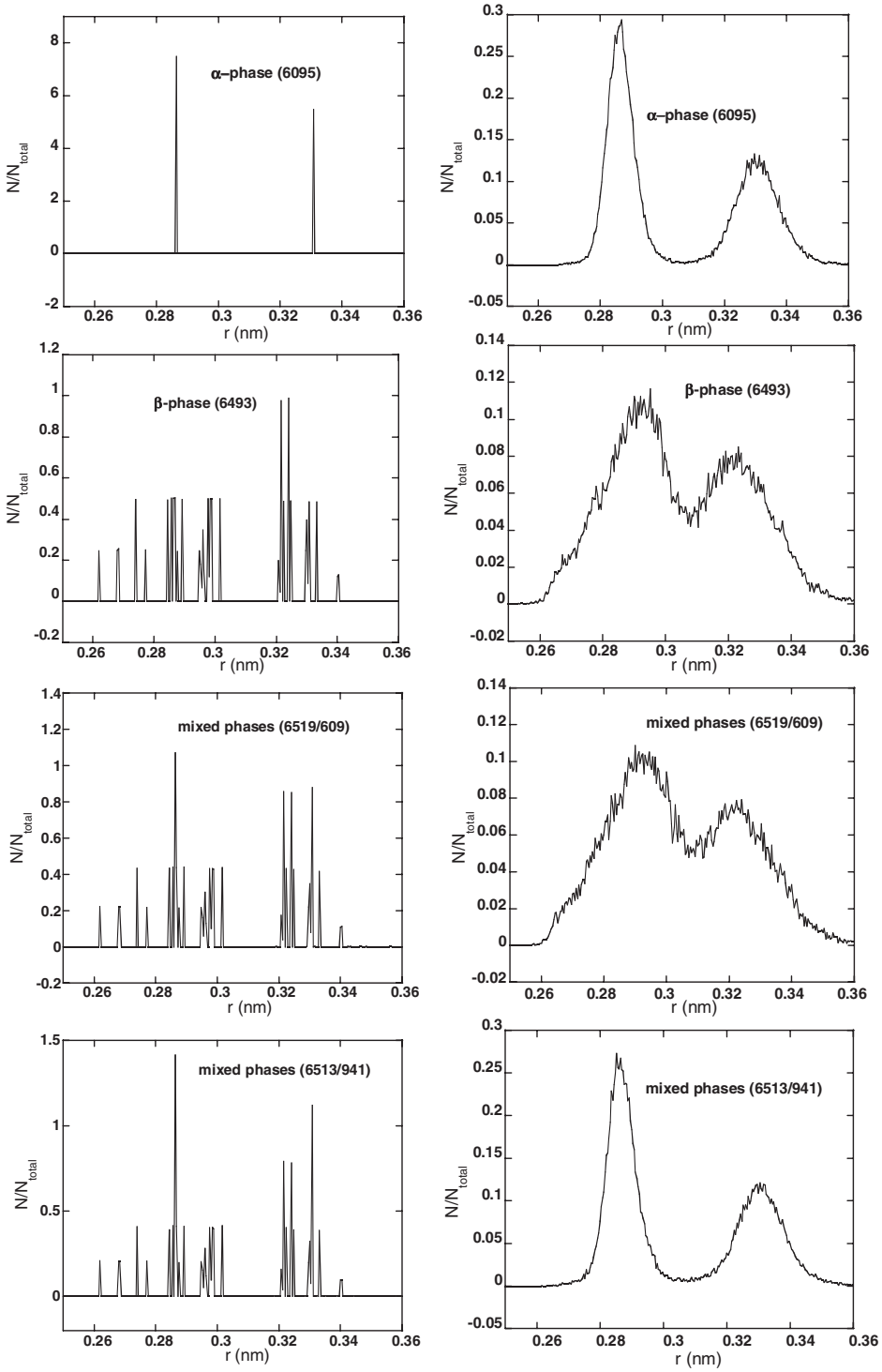

Figure 4. The radial distributions of initial and end structures of 6513/609 and 6513/941 clusters compared with those of the pure bcc 6095-atom Ta cluster (a rhombic dodecahedron) and a 6493-atom ball β-phase cluster relaxed at 1500 K. The cluster sizes are shown in parentheses.

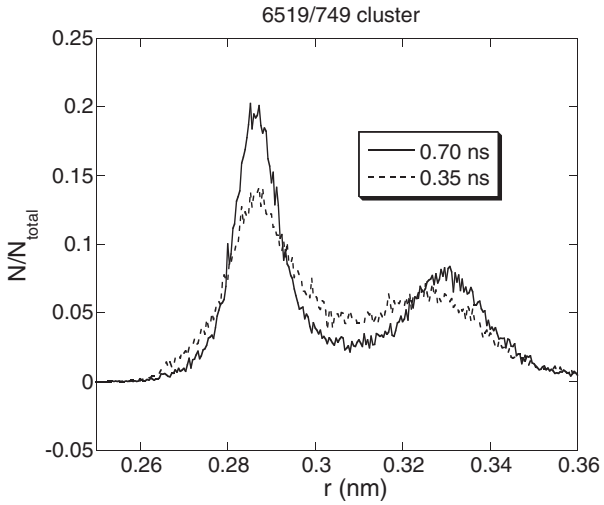

Figure 5. Comparison of radial distributions for 6519/749 cluster at 1500 K at times of 0.35 and 0.70 ns, respectively.

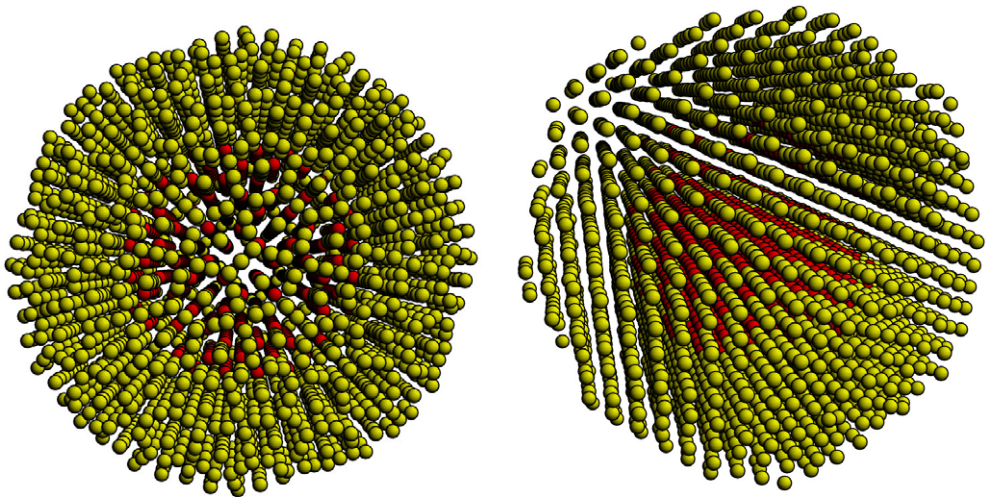

Figure 6. The visualization of the initial (left) and final (right) structures of 2983/531 cluster at 1000 K. The dark atoms correspond to the α-Ta central core.

(This figure is in colour only in the electronic version)

demonstrated by the slow decrease in energy (figure 3). The RDF (figure 5) shows that the structure at 0.70 ns has more bcc features than that at 0.35 ns, signifying a 'slow' β-to-α-phase change. A visualization of the 2983/531 cluster at 1000 K (figure 6) shows quite different atomic arrangements between the initial and end structures. Clearly, the disordered β-phase in initial configuration transformed to a well ordered bcc structure by the end of the simulation.

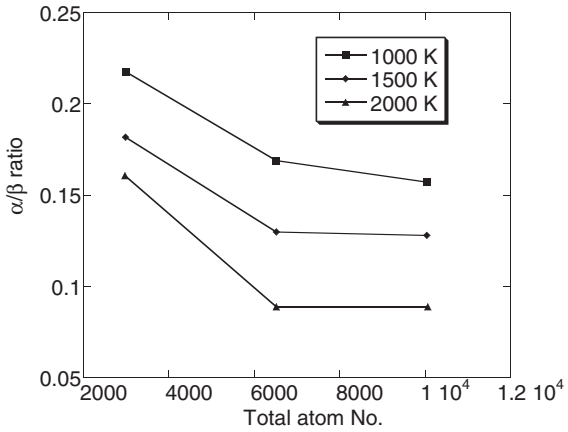

Figure 7. The critical α-to-β ratio for phase transformation as a function of cluster size at 1000, 1500 and 2000 K.

4. Discussion

The deposited β-Ta thin film undergoes phase transformation to α-Ta when it is heated to $\sim$800–1000 K [3–5]. In our simulations, we did not observe β-to-α-phase transformation for pure β-Ta clusters even at temperatures very close to the melting point. However, we observed phase transformations for mixed-phase clusters depending on the α to β atom ratio and temperature. The results of calculations on three cluster groups with different sizes are summarized in table 1. The table shows that the clusters exhibit a greater tendency to phase transformation at higher temperatures or with larger α-to-β-atom ratios. The incorporation of α-phase in β-phase can dramatically reduce the melting point of β-Ta clusters. The melting curve (figure 1) predicts that a $\sim$5000-atom pure β-Ta cluster would melt at $\sim$2400 K, but the 6513/941 cluster is transformed to pure bcc at 1500 K. Higher temperatures were sometimes needed in order to observe the phase transformation during a feasible simulation time. For example, no phase change occurs at 1000 K for a 6519/749 cluster in 3.5 ns, while at 1500 K it shows very slow transformation and at 2000 K phase change is complete in less than 1.0 ns. On the other hand, simulations show that the large α-Ta percentage can lower the temperature at which the phase starts transforming. At 1000 K phase change occurred for the 6513/1139 cluster (17.45% α-Ta) but not for the 6529/941 cluster (14.45% α-Ta).

The critical α-to-β ratio for phase transition depends on the temperature and cluster size. At a given temperature and for a given cluster size, the critical ratio should locate somewhere between the nearest two values corresponding to 'N' and 'Y' or '$\sim$Y', respectively, as indicated in table 1. The ratio, at which clusters start showing phase change behaviour (e.g., for the 6500-atom group, 0.1689 at 1000 K, 0.1289 at 1500 K, 0.088 88 at 2000 K) is considered a rough estimation of the critical ratio for phase transition, and was plotted as a function of cluster size for each temperature in figure 7. For a given temperature, the critical ratio decreases and tends to approach a limit as the cluster size increases. For the same size clusters, the higher the temperature, the lower the critical ratio. High temperatures do not guarantee phase change; the α-to-β ratio must be no less than the critical ratio. Phase transformation does not occur for 6519/411 and 10045/609 clusters in our simulation even at temperatures close to their melting points. It should be noted that the critical ratio values for phase changes could be only valid for the particular interfaces constructed in our mixed-phase clusters, as described in

section 2.3. The orientation of the internal α-Ta sphere with respect to that of β-Ta shell and truncation distances at the interface would affect the critical ratio value at a given temperature. However, the trends revealed in simulations should be correct for any other consistent interface constructions.

The phase transformation involves a change in the microstructure, which implies rearrangement of atoms via diffusion. Nucleation and growth are two required processes. Nucleation, a dominant process, involves the formation of very small particles, or nuclei formed at grain boundaries, defects. Once nuclei form, they grow in size at the expense of the surrounding material. For clusters with sufficiently large α to β Ta ratios, the incorporated α-Ta clusters can serve as nucleation centres. Increasing temperature can result in observable phase transformation over a finite simulation time. For clusters with low α to β Ta ratios, the α-Ta clusters are too small to provide adequate surface area.

The reported β-to-α-phase transformation temperatures are in a range of $\sim$800–1000 K, depending on deposition conditions [4, 5]. However, the phase transformation was not observed in simulations on pure β-Ta clusters [6] or extended solids [24], although the simulation time was long. The simulation work on mixed-phase clusters revealed that a particle containing small portions of α-phase Ta can undergo a β-to-α-phase change at low temperatures. The results suggest that thin films of β-Ta may contain very small grains of α-Ta, which play an important role in β-to-α-phase transformation. The mixed-phase construction is a simplified model based on the simple interface. However, the approach presented possibly describes the trends expected.

Indeed, x-ray measurements of β-Ta films revealed small amounts of the α-Ta phase [6, 18, 19]. On the other hand, Knepper *et al* recently reported that the addition of oxygen during deposition of β-Ta led to compressive stress increases and inhibited the phase transformation [25]. The grains in tantalum thin films are much larger than the clusters. The simulation on tantalum particles as large as grains would require extensive computational cost. However, based on the extensive molecular dynamics studies of metal clusters [26–29], the properties displayed by tantalum clusters should be qualitatively correct for grains. As reported in the literature, tantalum thin films are usually a mixture of two phases [6, 18, 19]. The phase in the minority sometimes may not be observed by x-ray diffraction, depending on the relative amount of both phases. High x-ray flux or long scan times may reveal very weak peaks from small α-Ta grains in the diffraction pattern of β-Ta films. Two very small α-Ta reflections (110) and (222) were observed in the diffraction pattern of a β-Ta film using a 55 h scan [6], but not in a 2 h scan pattern. The small α-Ta particles coexisting in β-Ta films can serve as nuclei or seeds for the nucleation, which greatly assists in the β-to-α phase change at temperatures as low as $\sim$800 K. Once nucleation is completed, the growth can proceed smoothly at lower temperatures.

5. Conclusion

Melting simulations show that β-Ta clusters have a lower melting temperature than the same size α-Ta clusters. No phase transformation was observed for pure β-Ta clusters up to their melting point, indicating the stability of the β-phase. Simulations of Ta clusters with mixed α- and β-phases revealed that a β-Ta cluster containing a small α-Ta cluster core induces the β-to-α transformation at temperatures far below the β-Ta melting point, depending on the cluster size and α-to-β-atom ratio. At a given temperature, the critical ratio for phase transformation decreases as the cluster size increases. For the same size clusters, the higher the temperature, the lower the critical ratio. These results suggest that the phase transformation at temperatures as low as $\sim$800–1000 K observed for β-Ta thin films is due to α-phase grains in β-Ta film grains.

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