

Lattice Parameters and Thermal Expansion of Zirconium Thin Films

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(Received 10 June 2013; published online 02 September 2013)

Using the molecular-dynamics method with many-body potential of interatomic interaction we have studied the polymorphism of zirconium thin films. The conditions for stability of metastable bcc(001) and fcc Zr films are determined at constant zero pressure. The dependences of the lattice parameters and thermal expansion coefficients on the temperature and thickness of bcc, fcc and hcp Zr films are calculated. The peculiarities of their variation near structural transformations are discussed.

Keywords: Thin films, Size Effect, Phase Transformation, MD Simulation.

PACS numbers: 68.55.-a, 68.60.Dv, 64.60.My

1. INTRODUCTION

The possibility of the formation of anomalous phases in thin films of transition d-metals, and the conditions for their stabilization have been discussed for quite a long time [1]. Such anomalous phases include polymorphous structures not observed in bulk samples, but stabilized in thin films. In [1] it was shown that whereas the bcc lattice is stable in bulk samples, a fcc structure can form in thin films, since the more closely packed phase has a lower surface energy.

It is well known, for example, that on the equilibrium P-T phase diagram for zirconium in macroscopic state the fcc phase is lacking, and three structures are realized: at low temperature and pressure an hcp structure (α phase) which with increasing temperature turns into a β phase with bcc lattice. At low temperatures an increase in pressure leads to a sequence of structural transformations: hcp $\rightarrow\omega\rightarrow$ bcc.

At the same time, there are experimental data on obtaining Zr thin films with fcc structure [2, 3, 4], as well as nanoparticles of polycrystalline fcc zirconium [5]. The possibility of the existence of a metastable fcc phase in zirconium was also suggested in a number of theoretical studies performed on the basis of ab initio calculations of the Gibbs energy [6] and molecular-dynamics (MD) method [7]. It should be noted that in different experimental studies the conditions for the fcc phase existence substantially differ depending on the experiment parameters.

In this work the MD method was used to investigate the phase size effect, the conditions for structural stabilization and new phase formation, the phase morphology, the mechanisms of phase transformations in Zr nanofilms. The peculiarities of thermal expansion of Zr thin films with different crystal structures were studied depending on the film thickness at constant pressure ($P = 0$).

2. CALCULATION METHOD

The structure stability and physical characteristics of Zr films were studied using the standard XMD package [8]. The many-body potential [9] constructed within

the "embedded atom" model was chosen to describe interatomic interaction in zirconium. This potential allows one to obtain, to a high degree of accuracy, the bcc and hcp lattice parameters of zirconium, cohesive energy, elastic constants, melting temperature, as well as the experimentally observed features of the Zr phonon spectrum and their changes with temperature, including the softening of the transverse N-phonon with decreasing temperature [10].

The MD simulation was performed in two ways: 1) the isothermal holding, i.e. the formation, at a specified constant temperature and constant pressure ($P = 0$), of a crystallite which then is hold for a time $t = 100$ ps in the state of free evolution, and 2) the slow cooling, i.e. the formation of a crystallite at a high temperature, holding for a time $t = 100$ ps, and then a slow cooling at constant zero pressure with a temperature step ΔT and a holding time no lesser than $t = 50$ ps at each new temperature. The time step was constant and equal to $\Delta t = 1$ fs. When simulating the phase transformations, the calculation in all variants started with the formation of a crystallite with perfect bcc structure of crystallographic orientation (001). The lattice parameter was chosen equal to its value in bulk bcc zirconium at the corresponding temperature. The film thickness N_z on the z axis varied from 5 to 30 bcc unit cells. In the x and y directions cyclic conditions were used with $N_{x,y}$ ($N_x = N_y$) ranging from 7 to 36 u.c. Thus we simulated thin films infinite in x, y, with free surfaces on the z axis.

3. PHASE TRANSFORMATIONS IN ZIRCONIUM FILMS

The calculations have shown that for the bcc (001) films there is a critical thickness $N_z = 17$ u.c. (~ 6.1 nm) at which the sequence of structural transformations and their mechanism substantially change. In what follows the films of thicknesses $N_z < 17$ u.c. and $N_z > 17$ u.c. will be referred to as "thin" and "thick", respectively. The bcc (001) thin films are unstable over the whole temperature range considered; they undergo structural transformations, the sequence of which is temperature dependent. In the temperature range $500 < T < 1300$ K the fol-

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lowing sequence of structural transitions is observed: $\beta \rightarrow \gamma \rightarrow \beta' \rightarrow \alpha$. Here β is the original bcc (001) structure, γ is an intermediate metastable fcc phase, β' is a twin bcc (110) structure, and α is a hexagonal phase. Besides, the modification of the final phase depends on whether $N_{x,y}$ (the number of cells in the basic crystallite along the x, y axes) is even or odd: at odd values of $N_{x,y} < 20$ u.c. there forms an orthorhombic α' phase, while at any even $N_{x,y}$ an α phase with ideal hcp lattice arises. In our opinion the α' phase formation is due to the lack of vibrations with wave vectors located near the point N ($\kappa = 1/2[110]$) of the Brillouin zone of bcc lattice, which are necessary for the $\beta' \rightarrow \alpha$ transition to be completed. At $T \leq 500$ K the γ phase remains stable in the system, and at $T > 1300$ K the β' phase does.

The dependence of structural transformations on the crystallite size in thick films is presented on the Temperature - Film thickness ($T-N_z$) phase diagram shown in Fig. 1. The areas of the final stable phases observed in thick films are marked on the diagram. Note that in thick films the orthorhombic phase did not arise, which is due to a change in the mechanism of the hexagonal phase formation. The structure rearrangement in this case occurs as a result of shear deformation and not by martensitic mechanism as in the thin films.

In thick films reorientation of the original bcc (001) lattice into the bcc (110) one takes place only at $T \geq 1400$ K, but there exists a sufficiently wide temperature range in which the initial β phase remains stable. At temperatures $400\text{K} \leq T \leq 700$ K the bcc (001) structure turns into a twin one (γ_{tw}), in which the fcc plates are separated, at the shear boundaries, by thin interlayers of hcp phase. With an increase in N_z the number of such sheared twin plates increases along with the portion of hcp phase. In films with $N_z \geq 32$ u.c. there forms a homogeneous α phase which can be considered as a limiting case where each plate of γ phase involves only two atomic layers, all plates being shifted relative to each other in the [112] direction.

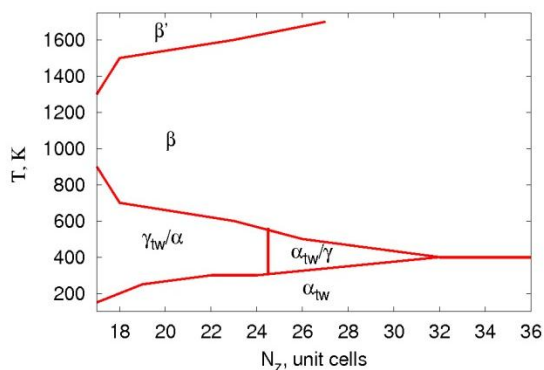


Fig. 1 – The $T - N_z$ phase diagram obtained by "isothermal holding" for thick bcc(001) Zr films: β' is the bcc(110), β the original bcc(001) phase, γ_{tw}/α is the twin fcc, α_{tw}/γ is the twin hcp phase with small fcc inclusions, α_{tw} is the twin hcp phase.

Thus in isothermal holding simulation the formation of α phase occurs, up to a critical film thickness (~ 6.1 nm), by the ordinary martensitic (wave) mechanism, while in films with a thickness greater than ~ 6.1 nm by the mechanism of shear deformation.

In simulation by the "slow cooling" technique the thin films were cooled from a temperature $T = 1500$ K, and the thick ones from $T = 1000$ K, in both cases with a temperature step $\Delta T = 10$ K and a holding time $t = 50$ ps at each new temperature. The calculation results are shown in Fig. 2. Here the film thickness N_z is plotted on the horizontal axis, the temperature on the vertical axis; in all computation variants $N_{x,y} = 24$ u.c. The temperatures of structural rearrangements are shown by different symbols. The films with $N_z = 5, 6$ u.c. after reorientation to the bcc (110) phase, completely transform at high temperature into the hcp phase; the temperature of this transformation is marked by the circles. In thin films with a thickness $N_z = 7-16$ u.c. the so-called "diffuse" transition bcc \rightarrow hcp is observed when the phase state changes not abruptly at one temperature value, but gradually over a certain temperature interval. The initial and final temperatures of such transformations are marked in the figure by the squares. A considerable difference in transition temperature is observed between the thin and the thick films, which is due to the fact that in thin films the transition proceeds through an intermediate bcc (110) structure, while in thick films it starts directly from the original bcc (001) phase. The films with $N_z = 17 - 24$ u.c. transform into a twin γ phase (crosses) by shear deformation in the [112] direction.

With further increase in the film thickness ($N_z \geq 25$ u.c.) the mechanism of transformations changes again. In this case the $\beta \rightarrow \alpha$ transition is realized by the mechanism of cooperative atomic displacements as in bulk zirconium. The film consists of alternating twin hcp regions oriented in accordance with long-wave vibrations arising at the given N_z dimensions (triangles). The thickness values obtained for films with a stable γ_{tw} phase (6.1-8.2 nm) agree with the results of ab initio calculations of the critical size of zirconium particles with energetically favorable γ phase (~ 6 nm) [6], as well as with the experimental data (5-10 nm) [5].

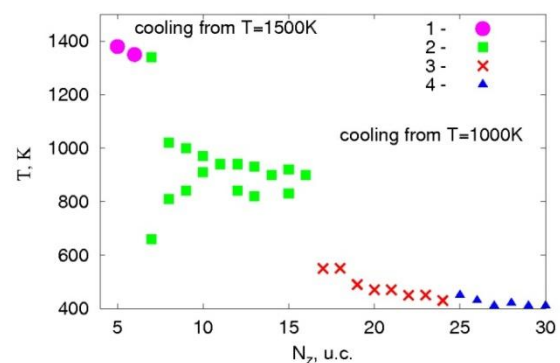


Fig. 2 – The temperature of structural transformations in bcc (001) films obtained by "slow cooling". 1 - the α phase, 2 - the diffuse $\beta' \rightarrow \alpha$ transition, 3 - the twin γ phase, 4 - the twin α phase. N_z is the film thickness.

Thus, the changes in the N_z parameter and temperature result in the formation of a fcc structure in the films at different ways of setting the temperature regime, while in the simulation of phase transformations in bulk zirconium this phase did not arise under any circumstances [11].

4. THERMAL EXPANSION OF ZIRCONIUM FILMS

After relaxation the bcc and fcc films lose the cubic symmetry and become tetragonal (bct and fct, respectively). Figure 3 shows the variation of the fct lattice parameters c (along the z direction) and a (along the x, y directions) with increasing film thickness. The calculations were performed for films of different thickness relaxed for 100 ps at $T = 300$ K with subsequent averaging over 50 ps. The c/a ratio is 1.042 for a film with $N_z = 5$ u.c., and 1.011 for $N_z = 30$ u.c., that is, the thinner the film, the greater is the tetragonal distortion of the lattice. The stable hcp and bcc (110) films differ from the metastable fcc and bcc (001) films in the fact that the interplanar spacing between the first and the second surface atomic layers diminishes in the stable films and grows in the metastable ones as compared to the interplanar spacing inside the film.

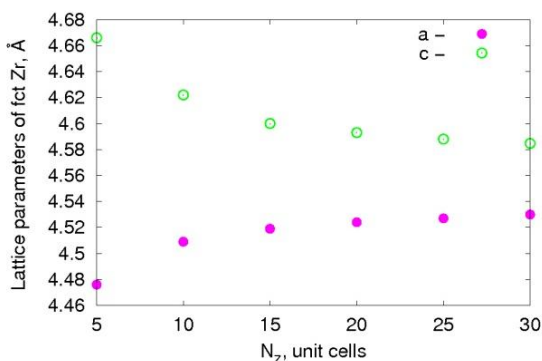


Fig. 3 – Variation of the lattice parameters (a and c) with the fct film thickness at $T = 300$ K.

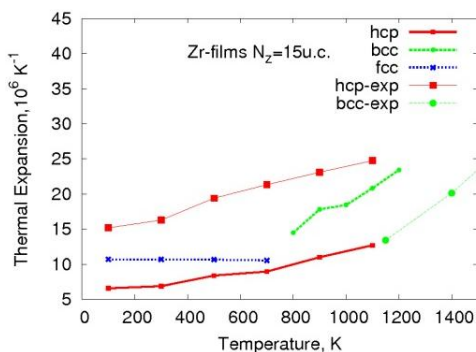


Fig. 4 – Thermal expansion coefficients for Zr films of thickness $N_z = 15$ u.c. with different structures. The experimental data are taken from Ref. [12].

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Figure 4 presents the calculated temperature dependences of the thermal expansion coefficients (TEC) for bcc, hcp, and fcc zirconium films with $N_z = 15$ u.c., along with the experimental data for hcp and bcc bulk samples. It can be seen that for hcp films the TEC is nearly half as large as in the bulk case. For bcc films the TEC values are greater than in the experiment. The thermal expansion coefficient of the fcc film slightly decreases with increasing temperature from $10.68 \times 10^{-6} \text{ K}^{-1}$ at $T = 100 \text{ K}$ to $10.52 \times 10^{-6} \text{ K}^{-1}$ at $T = 700 \text{ K}$.

The calculations performed for hcp films show that their TEC increases with the film thickness.

CONCLUSION

The MD simulation performed has evidenced the existence of a temperature range (depending on the film thickness) in which a metastable fcc phase can form in nanofilms of pure zirconium.

It is shown that the way of setting the temperature regime of MD simulation substantially affect the mechanism of phase formation.

A critical thickness of 6.1 nm is found for Zr films, at which the mechanism, sequence, and temperature of structural transformations do change. In films with a thickness up to 6.1 nm, the hcp phase forms by the martensitic mechanism, while in films thicker than 6.1 nm it arises as a result of shear deformation of fcc plates with the formation of an hcp structure at the shear boundaries. For odd values of $N_{x,y} \leq 20$ u.c., in films thinner than 6.1 nm there forms an orthorhombic α'' phase.

The lattice parameters in films depend on both the film thickness and temperature. The thermal expansion coefficients for the films and bulk samples have the same temperature dependence, but differ in magnitude.

ACKNOWLEDGMENTS

The authors acknowledge the partial support from Grants of the Presidium of the Russian Academy of Sciences №12-P-12-2010 and Ural Branch of Russian Academy of Sciences № 12-Y-2-1023.