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Thermal properties of fcc titanium and aluminum thin films

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ABSTRACT

The molecular dynamics method with many-body potential of interatomic interaction constructed in the embedded atom model is used to study the thermal characteristics of aluminum and metastable *fcc* titanium nanofilms with (001) and (110) surface orientation. It is shown that in Al films the linear coefficients of thermal expansion are positive in all the directions, except for the area close to the melting temperature. For fcc titanium the linear coefficients of thermal expansion in the film plane are negative in a wide temperature range. With increasing temperature, in Ti films the local vibrational densities of states of the surface atomic layers, polarized along the x, y, z axes, shift to the low-energy part of the spectrum only in those directions where a decrease in the lattice parameters is observed. The changes in the interface areas of Al films occurring with increase in temperature, lead to the growth of anharmonicity and a "softening" of the local vibration spectra near the critical temperature. It is shown that the negative coefficient of linear expansion is an indicator of the simulated system being in metastable state.

1. Introduction

In strongly anisotropic crystals, the linear coefficient of thermal expansion (CTE) α may be negative in one of the directions, but in the whole volume it is compensated and becomes positive. In this case, the resulting volumetric CTE, β, can be very low. Such materials exhibit a very high heat resistance. The thin films can also be assigned to anisotropic crystals. Moreover, it is known that polymorphic structures, not observed in massive samples, may appear in thin films. For example, a metastable *fcc* structure is realized in Zr, Ti, and Hf thin films [1–5].

On the other hand, in the experiments on metastable ZrW_2O_8 ceramics [6], a negative CTE was observed in a wide temperature range from 0.3 K to 1050 K. In another work by Evans et al. [7] it was shown that with Sn in place of Zr, the tin-containing analogue of the cubic material $ZrMo_2O_8$, i.e. $SnMo_2O_8$, expands when heated. These experiments indicate that zirconium plays a decisive role in the formation of negative coefficients of thermal expansion.

The understanding of atomic processes occurring in the interface layers of films of strongly anharmonic metals, such as Zr, Ti and Hf [8,9], being, in addition, in a "metastable" state and "forming" the behavior of these layers under changing external conditions, is of both fundamental and practical interest, because the unique properties of such materials can find new industrial applications. In [10] we have simulated the thermal expansion of *fcc* films of zirconium and obtained negative linear coefficients. In this paper we investigate the thermal expansion of *fcc* titanium films with surface orientations (001) and (110). The obtained thermal characteristics of the "metastable" *fcc* titanium films are compared with the analogous parameters in films of aluminum, for which *fcc* is the ground state. The relaxation of interface atomic layers is considered. The total and local vibrational densities of states, polarized along the axes x, y, z, are calculated at different temperatures, separately for the surface and interior atomic layers of the films. A comparison is made with the previously obtained thermal characteristics of *fcc* and *bcc* zirconium films.

2. Calculation method

The structural stability and thermal characteristics of Ti and Al films were studied by the molecular dynamics method, using the XMD package [11]. The interatomic interaction potentials for Ti and Al constructed in the embedded atom model [13] are taken from Ref. [12], where it was shown that these potentials make it possible to obtain, to a high degree of accuracy, the lattice parameters of *bcc* and *hcp* titanium and *fcc* aluminum, elastic constants, cohesive energy, melting temperature, and other physical characteristics for both pure Ti and Al and their various compounds.

In [14] we used these potentials to obtain the vibrational density of states (VDOS) for Al at various temperatures. Comparison with experiment shows that the selected potential makes it possible to describe the experimentally observed features of the aluminum phonon spectrum, including its shift to the low-energy region with increasing

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temperature, and therefore it can be successfully used in calculating the vibrational and thermal characteristics of aluminum films. In the same paper, the elastic moduli of *fcc* Ti and Al were calculated for both the bulk case and thin films. The calculation results show that all the elastic moduli of *fcc* Ti have positive values, which is indicative of the "virtual" stability of this structure and the possibility for simulating its properties. Note also a good agreement between the calculated lattice parameter of *fcc* Ti and the experiment [4], where titanium with *fcc* structure was deposited on a (0 0 1) Al film.

The films were simulated with cyclic boundary conditions along the x, y axes, and free boundaries along the z axis. The thickness of all films (along z) was 18 *fcc* unit cells, and along the x, y axes the size of the base crystallite was equal to 24 unit cells. In all cases simulation started with the formation of an ideal *fcc* lattice with the surface orientation (0 0 1) or (1 1 0) at $T = 10$ K. The system came into equilibrium for 500 ps at constant zero pressure with a constant time step of 1 fs. The base crystallite was heated with a step $\Delta T = 50$ K; at each new value the system relaxed for 100 ps. The methods for calculating the lattice parameters, CTE and VDOS at the selected temperature are described in detail in our paper [10].

3. Relaxation of the interface region and the film stability

After relaxation, the cubic symmetry of the *fcc* lattice turns to tetragonal and becomes the *fct* one. In Fig. 1 the total energy per atom is presented as a function of temperature for titanium and aluminum films of 18 u.c. in thickness. The curves for *fct* Ti films with (0 0 1) and (1 1 0) orientations, as well as for the *hcp* structure are presented in Fig. 1(a).

As seen from the figure, the *fct* titanium films remain stable in simulations over a wide temperature range. At a temperature $T = 1000$ K, in the (1 1 0) *fct* Ti film there occurs a transition to a twin structure in which strips with *hcp* and *fcc* structures alternate. Moreover, with a further increase in temperature, several "structure rearrangements" are observed: in these twin structures the thickness of the strips of different "phases" changes. At $T = 1400$ K the film loses stability. The *fct* Ti film with (0 0 1) orientation loses stability without any transitions at temperature $T = 1400$ K. Thus, as follows from our simulation, the *fct* Ti films are stable in a wide temperature range, but their energy lies above the energy of the *hcp* film. Since it is known from full-scale experiments that the fcc structure in Ti is stable only in films, it would be possible to consider the *fcc* titanium films to be metastable. However, in simulations, this difference in energy does not allow one to say with assurance whether this structure is metastable or merely less stable than *hcp* Ti. Especially considering that, as already mentioned, all elastic moduli of *fcc* Ti are positive for both the bulk crystallite and thin film, as shown in our calculations [14] and the first-principles studies [15–17]. Likewise, e.g., the energy of *bcc* Zr films is larger than that of *fcc* Zr (see Fig. 2 in [10]), but the *bcc* structure in zirconium is experimentally observed at atmospheric pressure and $T \geqslant 1136$ K, while *fcc* Zr can exist only in thin films.

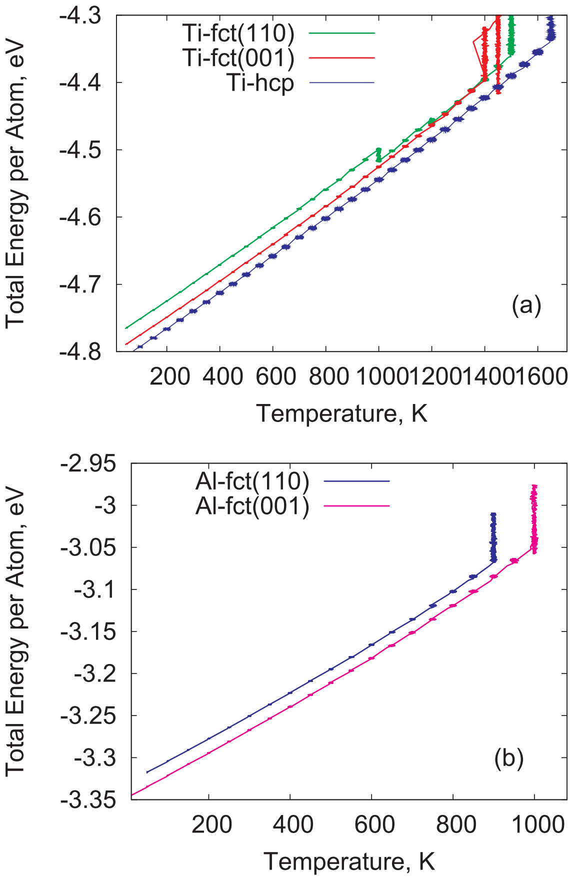

Fig. 1. Total energy per atom for the Ti - (a) and Al - (b) films as a function of temperature. All the films are 18 u.c. thick.

When "heating" aluminum films of the same thickness with orientations (0 0 1) and (1 1 0), we obtained the results shown in Fig. 1(b). As is seen, the aluminum film with (1 1 0) orientation is less stable, since its energy is higher and it loses stability at a lower temperature, i.e., the difference in energy does not allow to define whether the simulated system is metastable or stable.

The stability of the film is also significantly affected by its thickness and the processes occurring on the surface as a result of relaxation. Mechanical stresses always arise on the surface due to the difference in forces acting on the surface and inside the film. These stresses have a considerable effect on various properties of the film due to its structural features.

Fig. 2 show the averaged distances between atomic layers along the z direction for *fct* films of thickness 18 u.c.: (a) - Ti(0 0 1), (b) - Ti(1 1 0), (c) - Al(0 0 1), (d) - Al(1 1 0) at different temperatures after relaxation. As seen from the figures, in the interface region after relaxation, there are significant deviations from the average distance between the atomic layers, and the character of these deviations varies with temperature in different ways. Atomic layers, which are assigned to the interface region, are separated in the figures by vertical lines.

As can be seen from Fig. 2, at low temperatures the surface atomic layers of all the films are attracted to the film interior. At high temperatures, these layers in the Ti (0 0 1) film are moving away. This is apparently the cause of the film destruction at $T = 1400$ K without any structural transformations. A different picture is observed in the Ti film with the (1 1 0) surface: the surface atomic layers (the first and the second) are strongly forced against the interior, and this state does not change with increasing temperature, while for the interface atomic layers (the 3rd, 4th, and 5th), as the temperature rises, deviations of different sign from the average value of the interlayer distance along the z axis increase. At $T = 1000$ K, in the Ti (1 1 0) film there occurs transformation into a structure with alternating regions of *fcc* and *hcp* phases of different size.

Another situation is observed in *fct* aluminum films. Fig. 2(c and d) show the variation of the averaged distances between the atomic layers in the aluminum films with (0 0 1) and (1 1 0) orientation. One can see that in the case of (0 0 1) orientation (Fig. 2(c)), with increasing temperature the "profile" of the interlayer distances in the film does not practically change up to the highest values of temperature. At $T = 1000$ K, the film loses stability, at this temperature aluminum begins to melt. The Al(1 1 0) film is less stable, its energy curve lies higher (see Fig. 1(b)), it loses stability at $T = 900$ K. From Fig. 2(d) it can be seen that starting from $T = 700$ K the average distances between atomic layers in the interface area of this film begin to change.

When calculating the average value of the interlayer distance and, correspondingly, the lattice parameter along the z axis, only the atoms of the film interior, where there are no sharp changes in the interlayer