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Molecular dynamics simulation of surface melting behaviours of the V(110) plane*

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The modified analytic embedded-atom method and molecular dynamics simulations are applied to the investigation of the surface premelting and melting behaviours of the V(110) plane by calculating the interlayer relaxation, the layer structure factor and atomic snapshots in this paper. The results obtained indicate that the premelting phenomenon occurs on the V(110) surface at about 1800K and then a liquid-like layer, which approximately keeps the same thickness up to 2020K, emerges on it. We discover that the temperature 2020K the V(110) surface starts to melt and is in a completely disordered state at the temperature of 2140K under the melting point for the bulk vanadium.

Keywords: surface melting, V(110) plane, the modified analytic embedded-atom method, molecular dynamics

PACC: 6470D, 6155F, 6820, 6185

1. Introduction

The metallic surface plays a fundamental role in numerous applications and the behaviour of the surface melting is a best-known phenomenon of phase transition.[1−3] Recently, a number of problems related to the surface melting of metals have attracted many researchers' attention from theoretical[4−8] and experimental[9−11] views. About the phenomenon of the surface melting, a lot of work was dedicated to study of the specific[12−14] properties of the melting procession for some low index surfaces. And these investigations indicated that before the surface melting, a type of disorder called roughening was supposed to occur on several crystal surfaces firstly.[15−17] On the atomically rough surface, atoms still occupy the lattice positions, while the disordered surface has a liquid-like structure, also the liquid-like mechanical, and transport properties. As the temperature increases, the quasi-liquid film forms and the premelting phenomenon appears. And the surface-liquid film is affected by the underlying solid substrate, which is the reason why it is often considered quasi-liquid. However, other explorations showed that the Al (100) and Pb (111) did not show the premelting phenomenon on the surface.[18,19]

As mentioned above, there are still many different views about the problem whether the premelting and melting phenomena occur on some low-index surfaces under the bulk melting temperature. Hence the purpose of our present work is to contribute to the understanding of the atomic mechanisms underlying the theoretically and experimentally observed premelting and melting phenomena on the surfaces. Taking the V(110) plane with two free surfaces as an example, we have studied the surface premelting and melting phenomena in the whole temperature range from 0K up to the melting point using molecular dynamics (MD) simulations together with the modified analytic embedded-atom method (MAEAM). The paper is organized as follows: the calculation methods are shown in Section 2. Then the results and discussion are presented in Section 3. And finally the conclusions are given in Section 4.

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2. Description of the methods

In this study for the V(110) plane we have used a set of 2976 atoms distributed in 31 layers with 96 atoms per layer. We take [001] and [$\bar{1}$10] as x and y directions respectively and the two-dimensional (2D) periodic boundary conditions are used in x and y directions. And free boundary conditions in z direction, which is perpendicular to the (110) plane, are assumed. The crystal setup of a layer is shown in Fig.1. Interactions between V atoms are described with MAEAM, which have been successfully applied to the study of surfaces,[20] defects[21] and thermodynamic properties.[22,23] The model parameters for vanadium are listed in Table 1.

The present MD simulations,[24,25] where the six-value Gear predictor–corrector algorithm with a time step of 2fs is employed, are performed for the high-temperature properties of V(110) surface by heating slab-shaped samples from T=0K up to the bulk melting point in a canonical ensemble (NVT). We perform a constant temperature and constant pressure simulation (NPT) for a bulk system to calculate the lattice parameter at that temperature. The system of V(110) plane can then be created with these lattice parameter corresponding to the temperatures of interest. The free surface starts from T=0K and then moves on to each successively higher temperature from the well equilibrated sample at lower temperatures, in steps of 100K. Depending on the temperature, the samples are equilibrated by using 2×10^4 MD time steps at low temperatures and 3×10^5 MD time steps at high temperatures. The temperature of the system is controlled by a Nose–Hoover thermostat in the isothermal MD relaxation.[26,27]

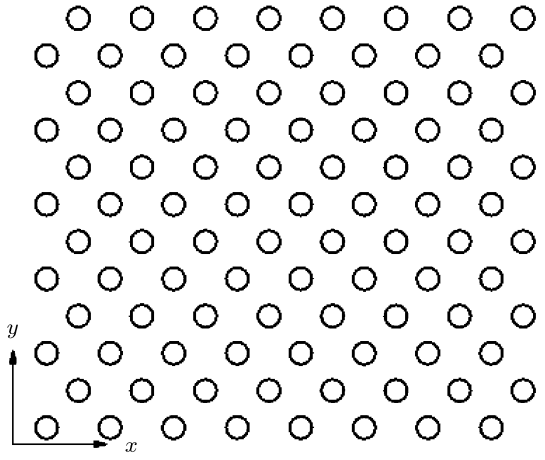


Fig.1. The geometry of one layer of V(110) plane. The 2D periodic boundary conditions are assumed in x[001] and y[$\bar{1}$10] directions.

Table 1. The model parameters of MAEAM for V(110) plane.

F_0/eV	n	α/μeV	k_1/eV	k_0/eV	k_1/eV	k_2/eV	k_3/eV	k_4/eV
3.278	0.730	–9.182	493.975	–476.769	229.643	–43.791	54.775	–258.123

3. Results and discussion

3.1. Surface relaxation of the V(110) plane

The interlayer relaxation[28] is calculated using the difference between the averages of z coordinate of the ith and (i+1)th layers,

$$d_{i,i+1} = \left\langle \frac{1}{n_{i+1}} \sum_{j \in i+1} z_j - \frac{1}{n_i} \sum_{j \in i} z_j \right\rangle, \qquad (1)$$

where z_i is the coordinate z of the atom i, n_i is the instantaneous number of atoms in the layer i, and the angular bracket denotes the time average. The distances between the neighbouring layers could be determined up to temperatures where surface premelting effects blur the distinction between individual layers. In this paper the surface relaxation at a given temperature is defined as

$$\Delta_{i,i+1} = \frac{(d_{i,i+1} - d_{\rm bulk})}{d_{\rm bulk}}. \qquad (2)$$

Here $d_{i,i+1}$ is the distance in the z direction between the ith and (i+1)th surface layers, and $d_{\rm bulk}$ is the interval between two neighbouring layers in the bulk. The relaxation of the four uppermost layer spaces d_{12}, d_{23}, d_{34}, and d_{45} are plotted versus temperature for the V(110) plane in Fig.2. At temperatures below the bulk melting point, the first layer exhibits an inward relaxation, i.e. the V(110) surface shrinks inward. At 100 K, the value of the first interlayer spacing d_{12} with respect to its truncated bulk position equals –4.01% of the bulk interplanar spacing $d_{\rm bulk}$.Upon heating, the contraction decreases nonlinearly to –3.29% at 1500 K. While the relaxation of the second interlayer spacing d_{23} are positive, implying that the second layer

expands outward, and those results of the relaxation for the third and fourth interlayer spacing d_{34} are almost equal to zero as the temperature is up to 1600 K. In brief, our calculated results for the relaxation are analogous with the subsistent ones at the equivalent temperature.[28] Unfortunately, efforts to gather more data points at temperatures higher than 1600 K have failed as it becomes increasingly difficult to determine accurately the distance between the first two layers due to frequent exchanges of atoms. Moreover, the stronger anharmonicity of the atoms vibration for the studied surface leads to a lot of vacancies and adatoms occurring at temperatures higher than 1600 K. If the relaxation of this surface is still calculated by the above formula, the results obtained for the relaxation are depressed. In terms of these facts, we can consider that it is the disordered atoms that induce the premelting phenomenon emerging on this V(110) surface at temperatures higher than 1600 K.

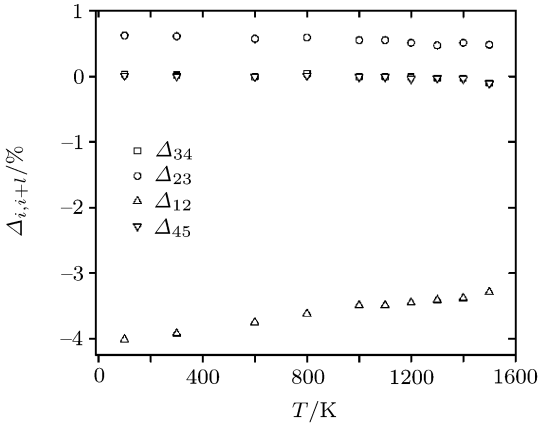


Fig.2. The relaxation of the four uppermost interlayer spacings $\Delta_{i,i+1}(i = 1, 2, 3, 4,)$ near the surface as a function of temperature for the V(110) plane. The sign $i = 1$ corresponds to the first layer, $i = 2$ to the second one, etc. The interlayer spacings Δ_{12}, Δ_{23}, Δ_{34}, Δ_{45} are denoted by the symbols of up triangles, circles, squares, and down triangles, respectively.

3.2. Layer structure factors for the V(110) plane

To further investigate the variation of premelting and melting processes of the V(110) surface with temperature, firstly we show, in Fig.3, the three uppermost layer structure factors of this sample, which are calculated in the equilibrium state, versus temperature changing from zero to near the melting point of vanadium. Here the layer structure factor is defined as[29]

$$S^2_{l,\alpha}((\vec{k}) = \left[\frac{1}{N_l}\sum_{i\in l}\cos(\vec{k}_\alpha \cdot \vec{q}_i)\right]^2 + \left[\frac{1}{N_l}\sum_{i\in l}\sin(\vec{k}_\alpha \cdot \vec{q}_i)\right]^2, \quad (3)$$

where $k_x = \frac{2\pi}{a}\left(\frac{\sqrt{2}}{2}, 1\right)$ and $k_y = \frac{2\pi}{a}\left(\frac{\sqrt{2}}{2}, -1\right)$, with a being the lattice parameter, and $\alpha = x, y$ are the reciprocal lattice vectors parallel to the (110) plane. The sum runs over the position vectors of atoms q_i, assigned to the lth layer. The symbol N_l denotes the number of particles per layer in the crystal. For an ordered crystalline, the layer structure factor for the plane is unity at zero temperature and approximately zero for a disordered layer near the bulk melting point. The calculated three uppermost layer structure factors for V(110) surface being equilibrated at the selected temperatures are shown in Fig.3. In this figure there are two horizontal dashed lines, where the value of the upper one is 0.5 and that of the other is 0.1. According to this, we experientially consider that the layer structure factors are lower than 0.5, which means that the layer configuration is in a partly disordered state, and those below 0.1 represents the plane is fully out of ordered state. For comparison, the variation of structure factors of the innermost layer with increasing temperature are shown also in Fig.3.

The structural evolution of the three topmost layers of the V(110) surface exhibits three stages, based on the above criteria (see Fig.3). First we note that in the low temperature region I (below about 1700 K) the in-plane structure factor decreases for the enhanced amplitude of atoms as the temperature rises, when these atoms are in the original position and the surface configuration is perfectly ordered. But in the uniform temperature case the first layer structure factor is lower than the factor of the other layers which are approximatively equal to each other. These facts show that the surface layer evidently influences the crystal structure and character. As the magnitude of the factor is below 0.5 in the region II, the system displays a prominent partially ordered state for the several layers of the surface. Therefore in this temperature region the surface is only partially disordered. In region III the structure factors are lower than 0.1 and the variations of their amplitudes are very small at 1950 K. The atoms in the first and second layers synchronously become disordered, which means that when the temperature close to the bulk melting point there is a quasi-

liquid layer on the surface, and the premelting phenomenon occurs on the V(110) surface. With increasing temperature the quasi-liquid layer slowly spreads inward and then leads to surface melting. On the contrary, in spite of the variation of the layer structure factors the innermost layer is always in an ordered state up to the melting point. At the temperature about 2100K the innermost layer structure factor falls abruptly, which can be interpreted by the long-range atomic interactions.[30] In the innermost layer there is no ordered-disordered transition for the (110) plane. In brief, the whole specimen has been melted entirely at 2140K below the melting point and the whole process of the surface melting is in good agreement with the previous experimental results.[10,11] In the light of the investigations above, we find that the temperature range of the premelting and melting transition is approximately from 1800 to 2100K, which is narrower than that of the fcc crystal.[8,31]

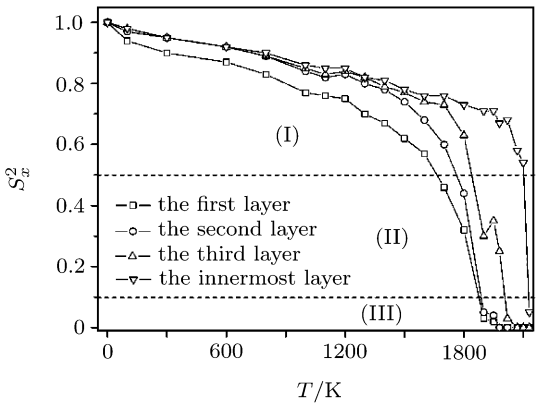
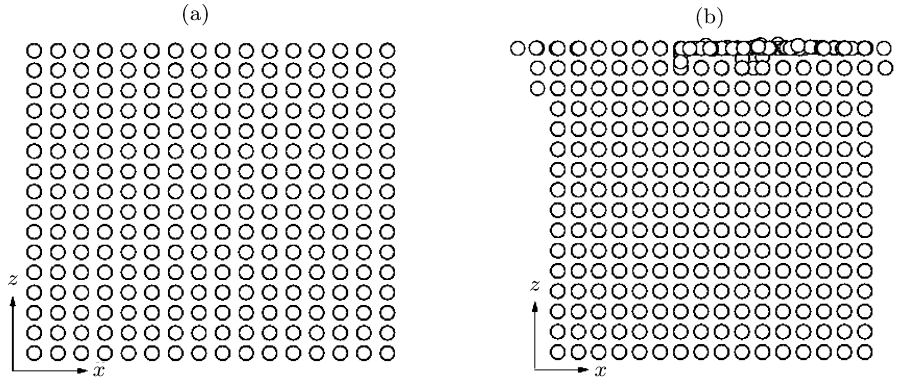


Fig.3. The layer structure factor as a function of temperature for the uppermost three and the innermost layers of the V(110) plane. The symbols of squares, circles, up triangles, and down triangles denote the first, second, third, and the innermost layers, respectively. The areas marked by I, II and III represent the ordered, partially and fully disordered regions, respectively.

3.3. Snapshot plots of the V(110) plane

In order to get a close sight of the quantitative analysis of premelting and melting that has been described in the foregoing discussions, we will next visualize our calculations by means of snapshots. Figure 4 shows a series of snapshots (schematic) of equilibrium configurations of the V(110) plane at selected temperature. The orderly configuration of the V(110) surface is preserved up to 1700K in Fig.4 (a). And then some disordered atoms begin to appear on the surface at 1800K (b), leading eventually to the in-planar partially disordered. Beyond this temperature the configuration of the first layer becomes completely disordered and the second layer structure keeps ordered partly, which indicates that a quasi-liquid layer comes into being and the premelting phenomenon occurs on the surface. In the temperature range from 1950 to 2020K the thickness of this quasi-liquid layer changes slightly. With increasing temperature the quasi-liquid layer obviously spreads inward, which means that the surface melting takes place in the (110) plane (see Fig.4(e)). Finally, the orderly crystal structure of the specimen disappears entirely at 2140K, which is a little lower than the bulk melting point of vanadium. The obtained results are similar with the previous experimental ones.[17,32−34]

In addition, as seen from Figs.4(b)–4(e), there is a partially disordered region between the quasi-liquid layer and the ordered structure. In the light of these facts, we conclude that the process of the V(110) surface melting can be divided into three stages, i.e. partially disordered, premelting and melting as the temperature increases.



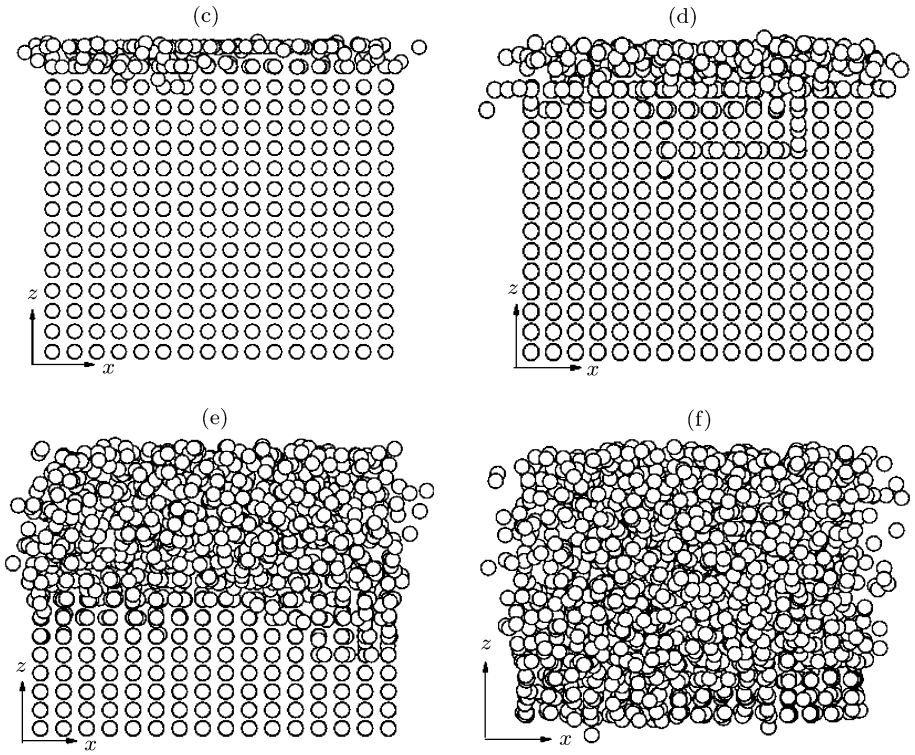


Fig.4. Schematic of snapshots for configurations of the V(110) plane at temperature (a) 1700K, (b) 1800K, (c) 1950K, (d) 2070K, (e) 2100K, (f) 2140K. The samples are viewed from [110]direction. The x and z axes denote the [001] and [$\bar{1}$10] directions, respectively.

4. Conclusions

In this paper, by calculating the interlayer relaxation, the layer structure factor and using the schematic of atomic snapshot, we have studied the surface premelting and melting behaviours of the V(110) plane by means of MD simulations and MAEAM. The partial disorder first appear on the surface at 1800 K or so, and then a quasi-liquid film forms, the thickness of which varies little up to 2020K, indicating that the premelting phenomenon occurs. Beyond this temperature the surface melting takes place on the V(110) plane. Finally, this plane melts entirely at 2140K slightly under the bulk melting point of vanadium.

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