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Atomic simulations for surface-initiated melting of Nb(111)

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Abstract: A modified analytic embedded-atom model(MAEAM) was applied to investigate surface premelting and melting behaviors of Nb(111) plane by molecular dynamics(MD) simulations. First the relaxation of surface interface space at 300 K was studied. Then a number *N* of the disordered atoms per unit area was determined at the given temperatures to investigate the surface premelting and melting evolution. The obtained results indicated that the premelting phenomena occurred at about 1 100 K and a liquid-like layer emerged on (111) plane simultaneously. As temperature increased up to 2 200 K, the number *N* grew logarithmically for short-range metallic interactions. Upon 2 350 K surface melting generated originally and the number *N* increased exponentially with the incremental temperature.

Key words: melting; premelting; Nb(111) plane; modified analytic embedded-atom model(MAEAM); molecular dynamics(MD)

1 Introduction

Melting is a best-known phenomenon of phase transition and the melting point is a primary parameter to understanding of the structure and properties of materials. Nevertheless, as a defect, surface severely influences the crystalloid configuration and performance. Thereby surface melting behaviors have attracted much attention. In recent years, great efforts on surface melting have been carried out by theoretical and experimental techniques[1−8]. Unfortunately, the detailed mechanisms and microscopic processes of melting have been incompletely understood yet. One of mysterious melting phenomena was that under normal conditions superheating of a solid is not observed[9−10]. For these cases, a possible explanation was that a liquid-like layer might already form on metal surface below the bulk melting temperature[1−2]. But on the microscopic level a comprehensive understanding of these melting phenomena has been kept much controversy.

In the past several decades, several theories were put forward to interpret the intrinsic mechanism[11] and extrinsic effect[12−13]. One of these theories was named Lindemann criterion in which the rigid physical quantity varies with temperature. The lattice mean field theory about surface melting was based on a free energy expression including the crystalline order parameters correctly. For example, TRAYANOV and TOSATTI[14] built a simplified but microscopic two-order parameter lattice theory for the melting based upon the average density, which effectively replaced the less manageable infinite set of crystalline Fourier components of the atomic density[1]. MD simulation provided a powerful tool to detect atomic-scale details in melting. The key to this method was how to determine the mutual potential of atoms correctly. Recently this method has been successfully used in many fields[15−20].

Hence, for the advantage of the MD simulation, in this work, MAEAM was used to study the temperature dependence of the crystalline configuration in order to explore the melting mechanics. By these, a quantificational description can be given about the melting evolution to eliminate the controversy in the field of the melting transition.

2 Method

The simulated calculations have been made with a slab. It was made up of 31 layers in *z*[111] direction and

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each of them had 96 atoms. The periodic boundary condition (PBC) has been imposed along $x[\bar{1}10]$ and $y[\bar{1}\,\bar{1}2]$ orientation to weaken the influence of the boundary on the interesting quantities, while two symmetrical surfaces perpendicular to z direction were kept free. Thus the length of the crystal was "infinite" in x, y directions and finite in z direction. The crystal setup of a layer is shown in Fig.1.

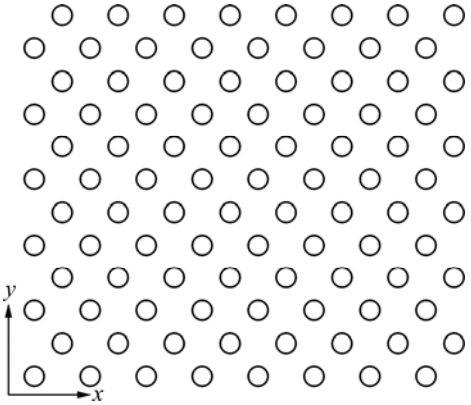

Fig.1 (111) plane geometry of one layer (two-dimensional(2D) periodic boundary conditions are used in $x[\bar{1}10]$ and $y[\bar{1}\,\bar{1}2]$ direction)

The MD simulations, where the six-value Gear predictor-corrector algorithm has been employed, were performed to study the melting of Nb(111) by heating slab-shaped samples from 0 K up to the melting point in the canonical ensemble. A constant temperature and pressure ensemble was used for a bulk system to calculate the lattice parameter at a given temperature. The slab was then created with the lattice constant corresponding to a given temperature of interest. The slab was started from T=0 K and then moved on to each successively higher temperature from the equilibrated sample. The sample was equilibrated by using 2×10^4 MD time steps in the lower temperature range and 5×10^5 MD time steps in higher temperature range. The temperature was controlled by a Nose-Hoover thermostat [21−22].

The interactions among metal atoms have been described by MAEAM, which has been successfully applied for the modeling of surfaces, point defects and thermodynamic properties[23−25]. The potential function has been described elsewhere in detail[25] and those model parameters of niobium are listed in Table 1.

Table 1 Model parameters of MAEAM for Nb(111)

F_0/eV	n	α/μeV	k_{-1}/eV	k_0/eV
4.963 7	0.70	−6.890 8	184.941 8	−851.405 4
k_1/eV	k_2/eV	k_3/eV	k_4/eV	
1 568.1 67 9	−1 442.302 7	660.119 1	−119.897 4	

3 Results and discussion

3.1 Surface relaxation of Nb(111) plane

The relaxation is defined as the change of surface-layer spacing from the bulk value. The calculated method for the relaxation is shown in the following equation[15]:

$$\Delta_{i,\,i+1}=(d_{i,\,i+1}-d_{\text{bulk}})/d_{\text{bulk}} \quad (1)$$

where $d_{i,\,i+1}$ is the distance in the perpendicular (111) plane direction between the ith and (i+1)th layer in surface region, and d_{bulk} is the distance between adjacent layers in the bulk. The thermal relaxation between the first and second layer has been calculated as listed in Table 2, where the previous results are also listed. The computational results were in excellent agreement with those obtained. The negative value of the relaxation revealed that the surface contracted inwards, which was caused by the broken metallic bonds of atoms in surface region.

Table 2 Surface relaxation of Nb(111) at low temperature (%)

TB-QMD[26]	TB[27]	FP-LMTO[28]	This work ($\Delta_{1,2}$) (300 K)
−21.5	−24.8	−9.4	−23.9

3.2 Disordering and melting zone of Nb(111) plane

To make sure the premelting phenomena occurring on the exposed face, the temperature dependence of the atomic configuration change of the (111) sample at 1 100 K and 1 800 K is detected, as shown in Fig.2. At 1 100 K, as shown in Fig.2(a), except for a few disordered atoms in surface region, the whole sample retains ordered lattice structure. This indicated that the surface grows rough only. Then from Fig.2(b), it was found that the entire layer atoms in surface region became disarranged and the near-neighbor adjacent layer atoms were located in their lattice positions. Thereby, it was assumed that as all atoms of one layer were in disordered state, its near-neighbor inner layer atoms kept in ordered state. Thus the premelting phenomenon occurred on the (111) surface firstly. In addition, the obtained results meant that starting with the outmost layer the disordered phenomena gradually overspread into the inner layers of the sample one by one. These behaviors were observed experimentally for Pb(110) and Al(110)[29−31]. Therefore, the transitional evolution of the (111) plane crystalline configuration was further explored by calculating the disordering atoms at the given temperature.

According to the simulated results, the number N of disordered atoms per unit area was counted at the selected temperatures running from 1 100 K to the

melting point of bulk niobium. The number N increased with the incremental temperature, which is displayed in Fig.3. The vertical and horizontal coordinate denoted the number N and the natural logarithm of the difference between the melting point and the given temperature, respectively. From Fig.3, it was found that the whole transitional process of the (111) slab included three steps, namely premelting, premelting-melting transition and melting stages labeled with A, B and C, respectively. These different zones were approximately separated by the vertical dashed lines.

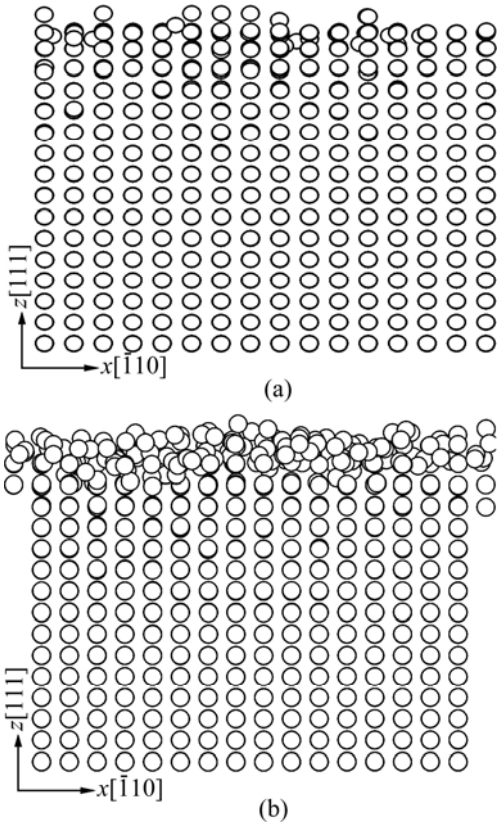

Fig.2 Atomic configuration of Nb(111) sample at 1 100 K (a) and 1 800 K (b)

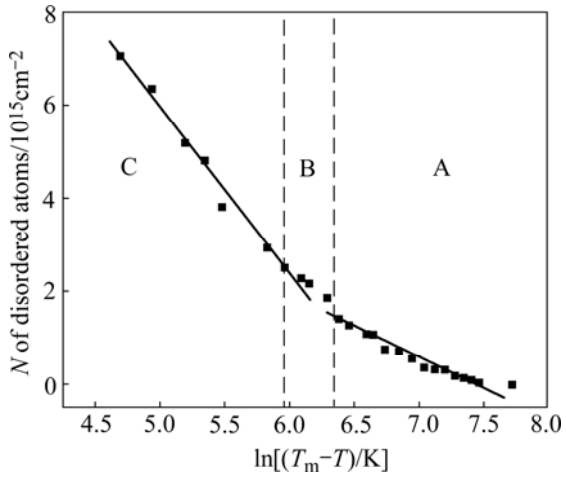

Fig.3 Change of number N with incremental temperature

3.3 Premelting mechanics of Nb(111) plane

According to the previous results supplied by PLUIS et al[3] and discussion above, in the zone A the simulated temperature dependence of N was further investigated, as shown in Fig.4. The number N with incremental temperature exhibited a logarithmic growth law, which was written as

$$N=\alpha+\beta\ln(T_m-T) \tag{2}$$

where α and β are the fitted constants and equal to 9.50 and −1.27, respectively. The parameter T_m is the bulk melting point of niobium. Based on the explanation given by PLUIS et al[3], the premelting process of a crystal with metallic bonding was well described as the slowly logarithmic increase at lower temperatures (1 100 K $\leqslant T \leqslant$ 2 200 K) because of short-range atomic interaction.

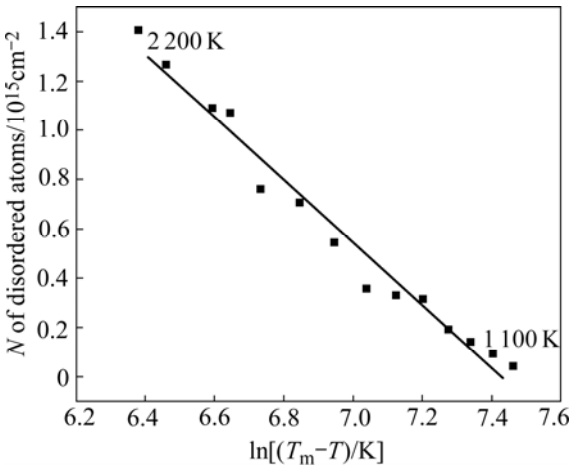

Fig.4 Number N of disordered atom with temperature increasing in premelting area A

From the disordered atomic number, the premelting atomic layers and the thickness of the quasiliquid film were estimated. The evaluated methods were described as

$$K=\frac{NS}{n_0} \tag{3}$$

$$l=Kd \tag{4}$$

where S is the real area of a (111) atomic layer, d is the spacing between two neighbor atomic layers, n_0 is the atom number in a (111) crystalline plane of our selected slab, and K is the number of the premelting atomic layer. Based on Eq.(3), K was approximately equal to 2.7 ($<$3 atomic layers) at 2 200 K, which meant that the third layer was in partially disordered state. Below this temperature the varied relation between the number of the premelting atomic layer and corresponding temperature was inconsistent with the fitted tendency, as shown in Fig.4. Then according to Eq.(4), the thickness

of the quasiliquid film was determined which was less than that of three atomic layers in the premelting temperature scope. These results indicated that the short-range atomic interactions played an important role in the premelting state.

3.4 Melting mechanics of Nb(111) plane

The temperature dependence of the disordered atoms in the region C is plotted in Fig.5, where the relation between them might be approximately expressed as

$$\ln N=\zeta+\xi\ln(T_m-T) \quad (5)$$

And the fitted parameters ζ and ξ are equal to 6.12 and −0.87, respectively. By changing the expression format of the formula, the relation took on an approximately power law as described by N—$(T_m-T)^{\xi}$. According to the viewpoint of the thermodynamic model [3], the thickness of the quasiliquid film in high temperature region was expected to grow in a power law when the thickness of the film became much larger than the range of the exponentially decaying short-range bonding and the long-range atomic interaction operated predominately. In these cases, only the weaker long-range dispersion forces remained. Hence, the power-law incremental disordered atoms occurred at the temperatures little lower than the bulk melting point of niobium. The obtained results accorded with PLUIS theory[2−3]. Moreover, the fitted power-law exponent ξ=−0.87 was reasonably equivalent to the reported result of FCC metal. The slight discrepancy maybe was initially derived from the following facts. First the (111) plane of niobium slab was completely melted at 2 630 K or so, which was a little lower than the bulk melting temperature. Thus near the melting point the disordered atoms were detected unsuccessfully. Secondly, at high temperatures the inharmonic oscillation of atoms was very prominent. The particular characteristic of the body-central cube crystalloid led to the different exponents. Based on Eqs.(3) and (4), the thickness of the molten layer was estimated. With the above discussion, the fitted results were in reasonable correspondence with the experimental ones given by PLUIS et al[3].

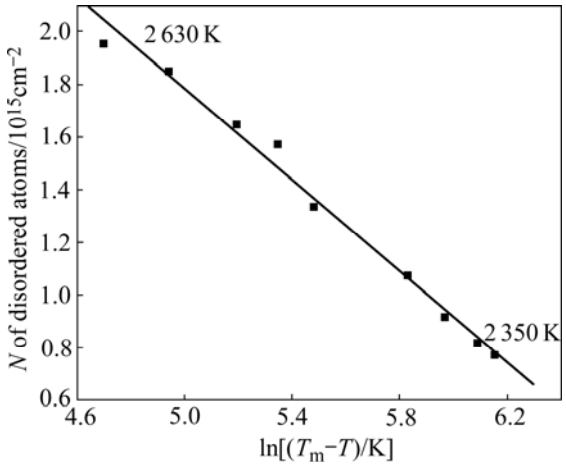

Fig.5 Logarithm of number N of disordered atom changed with temperature

4 Conclusions

1) According to the variation of surface-layer spacing of (111) plane at low temperature, the obtained surface relaxation of Nb(111) was in well agreement with the previous results.

2) As temperature varied from 1 100 K to 2 200 K in the premelting stage, the number N of the disordered atoms grew logarithmically as $N=\alpha+\beta\ln(T_m-T)$ for short-range metallic interactions, where β was about −1.27.

3) Upon 2 350 K the surface melting generated originally. N depended on temperature with a power law as $\ln N=\zeta+\xi\ln(T_m-T)$ for long-range interactions and the value of ξ was −0.87.

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