The superheated Melting of Grain Boundary

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Based on a model of the melting of Grain Boundary (GB), we discuss the possibility of the existence of superheated GB state. A Molecular Dynamics simulation presented here shows that the superheated GB state can realized in the high symmetric tilt GB. Whether the sizes of liquid nuclei exceed a critical size determined the superheating grain boundary melting or not. Our results also indicate that the increase of melting point due to pressure is smaller than the superheating due to nucleation mechanism.

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I. INTRODUCTION

The superheating has been found in a larger number of systems such as surface [1,2,3], small cluster [4], confined thin film [5] and particles covered (or embedded in) by material with higher melting point [6]. Generally, the melting of solid material is heterogeneous process with the nucleation mechanism at surfaces or interfaces [7,8]. Providing heterogeneous nucleation could be avoided by means of suitable coating [8] or internal heating [9], the metal crystal can be in the superheated state, its melting is completed by a thermodynamically instability resulting in homogeneous disordering and catastrophic mechanism with the stability limit from 0.2T_m to 2.0T_m [10,11,12,13,14].

A large number of researches have been contributed to the role of surface for the melting of crystal. The superheated melting of fcc(110) and fcc(100) surfaces are virtually never observed [15,16,17]. The only example of the superheated surface is the small crystal strictly confined by high-symmetry fcc(111) facts [1,2,3]. GB as another important quasi-2D defect also leads to the heterogeneous melting of solid material. Quite a number of studies have shown that GB can’t melt below the T_m (not pre-melting) [18,19,20,21,22,23,24,25,26,27,28,29]. Using the MD simulation, Kikuchi and Cahn, Ciccotti et.al. showed that GB doesn’t melt until temperature reaches to melting point of bulk. Nguyen et.al. using the more accurate interatomic potential by embedded-atom methods (EAM) studied the high-temperature GB structure, they found that, close to melting point T_m, the GB structure was disordered, quite liquid-like and meta-stable, and over a long interval of simulation the underlying crystalline order can re-emerge. The experiment (T.E.Hsieh and R. B. Balluffi) using the HREM (High Resolution Electron Microscopy) methods supported above arguments and showed that aluminum GB did not melt below 0.999T_m [30].

It is more surprising that some the simulations also hint that some high symmetric GBs similar to high symmetric surface can probably melt by the superheated [24]. In this work, parallel to Di Tolla’s work [16] for surface we study the possibility of superheated high-symmetry GB by a theoretical model and MD simulation of a symmetric aluminum GB.

When temperature beyond melting point a crystal reaches the superheated state, all liquid nuclei must be smaller than a critical size. These liquid nuclei are unstable and able to re-crystallize again. The liquid nuclei easily form at surfaces, grain boundary and other solid defects regions. So, to avoid larger liquid nucleus, the crystal must be prepared with the lowest number of solid defects. It’s easier to study the superheating of crystal in computer simulation than in experiment. We can construct perfect crystal using the periodic boundary condition in computer simulation. In experiment it’s very difficult to obtain infinite volume prefect crystal. We can’t eliminate the influence of surfaces, grain boundaries, dislocations and other defects with complicated structures. All these defects have potentially become the liquid nuclei to melt crystal. However surface effects can partially remove by coating other material with higher melting point or internally heating the material. By these methods we can obtain superheated crystalline grains.

Additionally, the grain boundary itself may probably become the liquid nucleus near the melting point of crystal. Based on our theoretical model, it’s possible that, under condition of the absent of critical nucleating cores, grain boundary doesn’t melt even the temperature beyond melting point. We hope to find the superheated grain boundary in computer simulation, although it is difficult to find in experiments due to different kind of unavoidable nucleation mechanism. Our simulation will show that high-symmetry grain boundary can sustain...
II. THE MODEL OF GB MELTING

The melting point $T_m$ of a solid may be defined as the temperature with the coexistence of solid phase and liquid phase. For a solid with surfaces or grain boundaries, the melting is generally completed by the mechanism of heterogeneous nucleation. We consider that a liquid film with thickness $2l$ forms between two semi-infinite solid (Fig. 1a). The change of free energy per unit area is taken as

$$\Delta F(l) = 2\rho L(1 - T/T_m) + \Delta \gamma(l)$$

where $\rho$ is the liquid density, $L$ the latent heat of melting, $\Delta \gamma(l)$ the difference between the overall free energy $\gamma_{SL-SL}$ of two interacting solid-liquid interfaces separated by a distance $l$ and the GB energy per unit area

$$\Delta \gamma(l) = \gamma_{SL-SL} - \gamma_{GB}$$

By extending the Cahn’s wetting theory to solid-solid interface [31], using $\Delta \gamma(0) = 0$ and only considering the short range interaction, we may obtain

$$\Delta \gamma(l) = \Delta \gamma_\infty(1 - e^{-l/\xi})$$

where $\Delta \gamma_\infty = 2\gamma_{SL} - \gamma_{GB}$ is the difference of the interface energy of two isolated solid-liquid interface $\gamma_{SL}$ and the GB energy $\gamma_{GB}$, $\xi$ is the width of solid-liquid interface.

The condition of GB melting is defined by following process. We may image there is a droplet in GB region (Fig. 1b), the equilibrium condition of the droplet is

$$\gamma_{GB} - 2\gamma_{SL}\cos(\theta) = 0$$

where $\theta$ is the wetting angle. If $\Delta \gamma_\infty > 0$, i.e. $\gamma_{GB} < 2\gamma_{SL}$, $\theta$ is a finite value, the droplet can survive in the region of GB (partial wetting), the whole GB can’t be wetted. As $\Delta \gamma_\infty < 0$, i.e. $\gamma_{GB} > 2\gamma_{SL}$, $\theta$ can’t be defined. A liquid film forms in GB region (Wetting) and the GB melts. Thus $\Delta \gamma_\infty = 0$, i.e. $\gamma_{GB} = 2\gamma_{SL}$ and $\theta = 0$, may be considered as the criteria of GB Melting.

In early time, one was decline to think that GBs melt below melting temperature, that is, at certain temperature below $T_m$, $\Delta \gamma_\infty < 0$. In this paper we only consider the possibility of GB superheated melting, that is, as $T > T_m$, $\Delta \gamma_\infty > 0$.

For superheated melting, the insert of Fig. 1c show that $\Delta F(l)$ has a local minimum at $l = 0$, and approaches to negative infinite as $l$ approach infinite. There is a maximum at $l_c$, which is

$$l_c = \xi \ln\left(\frac{\Delta \gamma_\infty T_m}{2L\rho \xi (T - T_m)}\right)$$

The Fig. 1c shows the temperature dependence of $l_c$. According to Fig. 1c), at a certain temperature $T(> T_m)$ and $l < l_c$, the system can reduce its free energy by decreasing the thickness of liquid film until the thickness reaches to zero, that is, the system crystallizes. When
$l > l_c$, the system can reduce its free energy by increasing the thickness of liquid film until the thickness reach to infinite, the GB melts. $l_c$ is the critical thickness at $T$. If at a temperature $l_c = 0$, any small thickness can lead to the melting of GB. The temperature is named as the maximum superheated temperature $T_s$, expressed as

$$T_s = T_m(1 + \frac{\Delta \gamma \xi}{2L_0 L_1^2})$$  \hspace{1cm} (6)$$

$l_c$ is also be expressed as

$$l_c = \xi L_0(\frac{T_s - T_m}{T - T_m})$$  \hspace{1cm} (7)$$

The critical nucleus is extremely large for $T \approx T_m$ and reduces rapidly with the increase of the superheating degree. At $T_s$, $l_c = 0$ (Fig. 1(c)) and the spontaneous melting happens. Between $T_m$ and $T_s$ the superheated states is meta-stable, although the melting doesn’t occur. In following several sections, by MD simulations of Aluminum GB melting and above model, we prove that GB can preserve crystalline even above $T_m$ until temperature reaches to the maximum superheated temperature $T_s$. Our simulation shows the behavior of superheating GB, that is, for $T_m < T < T_s$, there exists a critical width $l_c$ of liquid film. When the width of the artificially added liquid is larger than $l_c$, the GB melts, or the liquid film will reduce and the effect of crystallization is dominating.

III. THE MOLECULAR SIMULATION OF GAIN BOUNDARY

Molecular Dynamic simulations of crystal\cite{32} and high-symmetry surface\cite{16} have shown the superheating crystal without critical nuclei such as point defects and liquid drops. By internal heating, crystal with high-symmetry fcc(111) surface will be superheating. This is because the process of nucleation is homogeneous in the surface region. For some low symmetry surfaces such as fcc(110) surface, the anisotropy leads to heterogeneous nucleation and high concentration of defects, superheating is extremely difficult to achieve.

Reconstruction and roughening are two main structural transitions for a surface when increasing temperature. Behavior of grain boundary is more complicated than surface, including the migration, bending, sliding, zigzag and faceting transition. Our simulations show that it is difficult to control the homogeneous nucleation in computer simulation to obtain superheated grain boundary. However we can use symmetric grain boundary to make atoms homogenously distribute in GB region. Instead of periodic boundary, we have fixed two boundaries of simulation cell parallel to GB plane to decrease the possibility of grain-boundary sliding.

In this work we choose Al symmetric Σ13 (320) [001] tilt grain boundary Fig. 1(d) as our simulation cell with mis-orientation 67.8°, the tilt axis of the boundary is along the Z direction, the fixed boundary-conditions is used in the X direction perpendicular to GB plane, and periodic boundary condition are used in the Y and Z directions. The widths along X, Y, Z are 100 Å, 43 Å, 12 Å respectively. Interatomic potential plays the most important role in molecular dynamics simulations. In this paper, by using a more realistic potential, a Glue potential developed by F. Ercolessi and J. B. Adams\cite{33}, The glue potential has been used in a large number of the simulations of surface, cluster, liquid, and crystal, and the simulation results are perfectly consistent with experimental results\cite{1, 16, 34, 35, 36}. The lattice constant $a_0$ for Al at 0K is 4.032 Å. For the glue potential the melting points is about 936K\cite{37}, which is close to the experimental melting point of Aluminum (about 933K). The MD simulations are carried out at constant temperature, constant volume and constant atomic number. The time step is 0.06 (about 0.003psec), at each temperature the runs are made about 20000 time steps (about 60psec).

The static structure-factor $S(K)$ for specific reciprocal-space vector $K$ (Eq. 8) represents a quantitative measure for the long-range order and can be used as order param-

![Graph](image_url)
FIG. 3: The configuration of GB at high temperature. (a) The GB structure at 850K (high temperature disorder state) (b) The GB structure at 1050K (melting state) (c,d) The GB structure at 975K (superheated state) with unstable liquid film.

Parameter describing the transition between disorder and order.

\[
S(K) = \langle | \sum_{i \in GB} \exp(iK \cdot \mathbf{r}_i(t)) |^2 \rangle / N_{GB}^2 \tag{8}
\]

\(\mathbf{r}_i(t)\) is the position of \(i\)th atom at time \(t\). \(\langle \cdots \rangle\) is indicative of the time average. \(N_{GB}\) is the number of atoms in grain-boundary region. For a crystal the \(S(K)\) is approaching 1, for liquid it approaching to 0.

In order to study the stability and the nature of disordered grain-boundary, we define a distribution function of \(P(S)\) which is the statistics of the value of \(S(K)\) \((K = \frac{2\pi}{d} (0, 0, 1))\) of all molecular-dynamics time steps. Fig. 2 shows the distribution functions at several temperatures from 400K to 1050K. The centers of the peaks represent the degree of disorder and order, the widths of the peaks as a measure of the fluctuation of \(S(K)\) represent the instability of the GB structure. From Fig. 2 the peak is very narrow and the center of the peak is very near 1 in low temperature regime \((T \leq 400K)\), and this implies that the structure of grain boundary is very order and stable in low temperature regime. At 850K, the peak is board (the minimum is at about 0.5 and the maximum is at about 0.9), and this implies that the structure of grain boundary is disordered in this temperature. At about 950K, the width of peak is extremely board (the minimum reaches 0.1 and the maximum still retains at about 0.9), the fact implies the structure of grain boundary is rather unstable, sometime the structure of grain boundary is rather disorder like liquid because of the \(S(K)\) approaching 0, and sometimes it just likes a crystal structure with long range order because of the \(S(K)\) probably approaching 1. This shows that at this temperature the coexistence of liquid phase and solid phase is reached. Above results show that the melting-point of this system is very close to 950K. In our simulation, the large \(S(K)\) fluctuation near 950K just indicates the signal of solid-liquid phase transition. At 1050K the peak moves to the left and become narrow. The position of the peak is close to zero, the GB is melting. Our results also show that the maximum superheated temperature \(T_s\) is close to 1050K. We also calculated the pair correlation functions \(g(r) = \frac{1}{4\pi\rho N} \langle \sum_{i \neq j} \delta(r - r_{ij}) \rangle\) at various temperatures which show the liquid behavior at 1050K. Fig. 2(a,b) illustrate the GB structures at 850K and 1050K.

Our model shows that between \(T_m\) and \(T_s\), GB will enter a new superheated state of GB. The new state is characterized by (1) the coexistence of liquid and solid; (2) the smaller size of liquid nucleus than that of the critical nucleus at that temperature prevents from the melting of GB although \(T > T_m\). Fig. 2(c,d) show the competition of liquid and solid phase at 975K in superheated state. Sometimes there exists a liquid-like layer in the
FIG. 4: The response of superheated state for adding liquid film. (a,b) at 850K, \(2l=30\text{ Å}\). (c,d) at 975K, \(2l=20\text{ Å}\). (e,f) at 975K, \(2l=30\text{ Å}\).

grain-boundary region (c) but it is meta-stable and may disappear and crystalline phase re-emerges at following time steps (d). We will show that the superheated state (975K) is rather different from the high-temperature disordered state at 850K.

A liquid layer as the melting nucleus can be artificially added to the GB region by following methods: At a certain temperature \(T\), we sample some layers with width \(2l\), the atoms in these layers are heated up to an appropriate temperature \(T_a(>T)\) until a liquid layer forms. By allowing all atoms relaxation at temperature \(T\) again, we can obtain a new equilibrium structure at temperature \(T\). Fig. 4 shows that both the initial GB configurations Fig. 4(a,c,e) having already added a liquid film with widths \(2l\) and the final equilibrium configurations Fig. 4(b,d,f) at 975K and 850K respectively. At 850K, for \(2l=30\text{ Å}\), the liquid layers disappears after the relaxation about 50ps Fig. 4(a,b). However at 975K for \(2l=20\text{ Å}\), the liquid layer disappears Fig. 4(c,d)and for \(2l=30\text{ Å}\) the layer of liquid is still existent Fig. 4(e,f) after relaxation about 50ps. Therefore, we can obtain \(20\text{ Å} < 2l < 30\text{ Å}\) at \(T=975\text{ K}\).

Above results also show that the superheated state (975K) is very different in nature from the high temperature disorder state (850K). For high temperature disorder state, the liquid film can’t induce the melting of GB, but for superheated GB state, the GB melts only when the width of liquid film is larger than a critical width \(l_c\). In order to define the correlation length \(\xi\) and the thickness of liquid film, we calculate the atom density profile corresponding Fig. 4(f). Our results show that at 975K, the critical width \(2l_c\) is between 20Å and 30Å and \(\xi = 10\text{ Å}\), thus \(1.0 < l_c/\xi < 1.5\), which is consistent with the theory model \(l_c/\xi = 1.4\) with \(T_m = 950\text{ K}\) and \(T_s = 1050\text{ K}\) in
IV. DISCUSSION AND CONCLUSION

In summary, we study the possibility of superheated GB state by both a theoretical model and MD simulation. Our results indicate that we can obtain superheated grain boundary by having properly controlled homogeneously nucleating precession when increasing temperature. If there are liquid nuclei whose sizes are larger than a critical size the superheated grain boundary melts. Or the grain boundary waits for homogeneously melting when temperature higher than maximum superheated temperature.

We must justify that pressure plays important roles for the superheated in experiments and computer simulations. In experiments, both coating with high-melting-point materials and heating internally induce the internal pressure in melting region. In our simulation also there is internal pressure in melting region because the size of simulation cell doesn’t change companying with the increasing temperature. In this paper we only consider the superheating state due to the nucleation mechanism. The pressure mechanism and nucleation mechanism become intertwined and influence the melting of materials. Pressure lead to the increase of melting points. The melting point is about 950K in our simulation and higher than the experimental melting points $T_{exp}=933K$ and $T_{glue}=936K$ in simulation using glue potential without internal pressure. Pressure increases melting point less than $T_m-T_{glue} \sim 14K$. However the nucleation mechanism leads to the superheating about $T_s-T_m \sim 100K$.

The proximity effects of the superheated grains are also important to induce the superheated grain boundary sandwiched between two properly superheating grains. Because superheated state is meta-stable state in phase diagram, we don’t expect it’s long-live. The superheated materials melt by the nucleation mechanism or homogeneously melt at higher temperature.

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