Homogeneous Nucleation Catastrophe as a Kinetic Stability Limit for Superheated Crystal

K. Lu*
State Key Laboratory for RSA, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015, China

Y. Li
Department of Materials Science, National University of Singapore, Singapore 119260
(Received 16 December 1997)

Homogeneous nucleation kinetics for melting in superheated crystals is analyzed in order to derive a kinetic stability limit for the crystal lattice above its equilibrium melting point ($T_m$). It is found that at a critical temperature ($T_m^s$, which is about 1.2$T_m$ for various elemental metals) a massive homogeneous nucleation of melting occurs in the superheated crystal. Such a homogeneous nucleation catastrophe, which occurs before other proposed (rigidity, volume, and entropy) catastrophes can intervene, provides us with a kinetic stability limit for superheated crystals. [S0031-9007(98)06099-2]

PACS numbers: 64.70.Dv, 64.60.Qb

The melting process of crystalline materials has been experimentally proved to be nucleated at heterogeneous nucleation sites such as grain boundaries or free surfaces [1,2]. Providing heterogeneous nucleation can be avoided for melting by means of experimental techniques, crystals can be superheated above their equilibrium melting points [3–5]. Several attempts have been made in recent years to estimate the upper limit for superheating in crystals. Drawing on Kauzmann’s idea on the glass transition [6], Fecht and Johnson [7] proposed a thermodynamic stability limit for the superheated crystal in terms of an entropy catastrophe that occurs at a critical temperature ($T_s^c$) when the entropy of the superheated crystal equals that of the liquid phase. Later, Tallon [8] suggested an elastic instability limit for superheated crystals based on a rigidity catastrophe, a temperature at which a shear modulus in the crystal falls to zero. It was demonstrated that the upper limiting temperature for crystals due to the rigidity catastrophe $T_m^r$ is below the instability limits defined by the volume or isochoric catastrophe [8] ($T_m^c$, at which the volume of the crystal equals that of the liquid) and the entropy catastrophe ($T_s^s$). However, the superheating observed experimentally in metallic crystals (of which the highest is about 0.1$T_m$; $T_m$ is the equilibrium melting point) is evidently far below these proposed instability limits that range from 0.3$T_m$ to 2.0$T_m$. It is, therefore, of great significance to search the crucial process of melting that intrinsically limits the structure stability of the superheated crystal lattice.

In the superheated crystal where heterogeneous nucleation for melting is avoided, homogeneous nucleation might play a dominant role in the melting kinetics. In this Letter, we present a kinetic analysis of homogeneous nucleation behavior for melting in superheated crystals. It is found that in a superheated crystal a massive homogeneous nucleation catastrophe occurs at a critical temperature ($T_m^K$) where is much lower than the various instability limits ($T_m^r$, $T_m^c$, and $T_s^s$) proposed earlier.

When a crystal is heated above its equilibrium melting temperature ($T_m$), there is a driving force for melting from the Gibbs free energy difference between the two states, $\Delta G_v = G_l^f - G_s^f$. If the heterogeneous nucleation of melting can be avoided at grain boundaries, dislocations, or free surfaces by means of a suitable coating [3], or heating internally [9], only homogeneous nucleation of melting inside the bulk crystal will occur. To form a liquid spherical nucleus (with a radius $r$) inside a perfect crystalline lattice, the Gibbs free energy change will be

$$\Delta G(T) = \frac{4}{3} \pi r^3 (\Delta G_v + \Delta E) + 4\pi r^2 \gamma_{sl}$$

in which $\gamma_{sl}$ denotes the solid/liquid interface energy (which is assumed to be temperature independent) and $\Delta E$ is the change in strain energy density (per unit volume) resulting from the volume change upon melting. By analogy with the classical homogeneous nucleation theory for solidification [10], a critical size of $r^*(T)$

$$r^*(T) = \frac{-2\gamma_{sl}}{\Delta G_v + \Delta E}$$

and a critical work of nucleation

$$\Delta G^*(T) = \frac{16\pi \gamma_{sl}^3}{3(\Delta G_v + \Delta E)^2}$$

can be obtained for the homogeneous nucleation of melting. $\Delta G_v$ can be approximated by $\Delta H_m(T_m - T)/T_m$ (here $\Delta H_m$ denotes the fusion enthalpy change) by neglecting the heat capacity ($c_p$) difference between solid and liquid, as measurement results have indicated that $c_p$ of the crystal and liquid becomes equal within 100 °C of the melting point [7]. According to Allen et al. [11],

$$\Delta E = \frac{18\mu K e^2 f}{4\mu + 3K},$$

where $\mu$ is the shear modulus and $K$ is the bulk modulus for the solid, and $f$ is a factor to account for the effect...
of a free surface on the strain energy density which is taken to be 1.0 in the present case. $\varepsilon$ is the hydrostatic strain associated with the fractional volume change during melting ($\Delta V/V_c$), $\varepsilon = \frac{1}{\gamma} \Delta V/V_c$.

The homogeneous nucleation rate of liquid is a function of temperature consisting of a driving force term and a diffusivity term,

$$I_{\text{hom}} = I_0 \exp \left( -\frac{\Delta G^*(T)}{kT} \right) \exp \left( -\frac{Q}{kT} \right), \quad (5)$$

where $Q$ is the activation energy for atomic diffusion in the crystal lattice, and $I_0$ is a prefactor related to the vibration frequency of the atoms and the surface area of the crystal nuclei. According to Turnbull and Fisher’s treatment of solidification [12], $I_0$ is approximated by $nkT/h$ ($n$ is the number of atoms in a unit volume, $k$ is Boltzmann’s constant, and $h$ is Planck’s constant) by assuming that the same atomic transport behavior is relevant during melting above $T_m$ and freezing below $T_m$.

By means of the available data for $\Delta H_m$, $\gamma_{sl}$ (data from Ref. [13]), $K$, $\mu$, $\Delta V/V_c$, $T_m$, and $Q$, one can calculate the homogeneous nucleation rate of melting in superheated crystals. Figure 1 shows the calculated results of the nucleation rate as a function of temperature for aluminum, compared with that of the nucleation rate of solidification. It is seen that the homogeneous nucleation rate for melting increases by orders of magnitude from essentially zero to very high values over a narrow temperature range, i.e., there is effectively a critical temperature $T^K_m$ at which an “explosive” homogeneous nucleation for melting occurs inside the superheated crystal lattice. The critical superheating temperature required to give one nucleus per second per cm$^3$ under homogeneous nucleation of melting in Al was found to be 1127 K, which is about 1.21$T_m$. The critical superheating for such a homogeneous nucleation catastrophe, $\Delta T^K_m = T^K_m - T_m$, is found to be about 0.20$T_m$ ($\pm 0.02T_m$) for those elements listed in Table I, except the low-$T_m$ metals such as Sn and Pb. It is seen that the absolute values of superheating for melting $\Delta T^K_m$ are comparable to the undercooling for freezing (normally about 0.2$T_m$ for metal elements [13]), since the same solid-liquid interfacial energy is relevant in each case.

The explosive homogeneous nucleation of melting is similar to that for crystal nucleation in an undercooled liquid, but a fundamental difference exists between them. For crystal nucleation in an undercooled liquid, an increase in undercooling elevates the driving force but reduces the atomic diffusivity, resulting in a substantial increase in the nucleation rate at a critical undercooling ($T^K_m$) followed by an obvious decrease after its maximum value. For melting nucleation in a superheated crystal, however, an increase in superheating will enlarge both the driving force and the diffusivity, leading to a monotonic increment of the nucleation rate. It is expected that the nucleation rate for homogeneous melting will not decrease as the temperature rises farther.

From a kinetic point of view, the critical temperature ($T^K_m$) is considered as an upper limit for the superheated crystal, above which catastrophic melting will be initiated by massive homogeneous nucleation. For Al, $T^K_m = 1.21T_m$ which is much lower than the instability limits defined by the entropy catastrophe [7] ($T^s_m = 1.38T_m$), the volume catastrophe [8] ($T^v_m = 1.29T_m$), and the rigidity catastrophe [8] ($T^{s_{rig}}_m = 1.24T_m$). Lele et al. [14] proposed an alternative way of estimating $T^K_m$ and obtained even higher values for $T^K_m$ as much as 2.0$T_m$, in alkali metals. The instability temperature limit defined by

![FIG. 1. Calculated results of the nucleation rates for melting and solidification in the element aluminum. The characteristic stability limits ($T^{s}_{m}, T^{v}_{m},$ and $T^{s}_{m}$) are indicated (see text).](image)
TABLE I. Calculated results of the absolute and relative critical superheating required to give one nucleus per second per cm$^3$ for homogeneous nucleation of melting in various elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_m$ (K)</th>
<th>$\Delta T^K_m$ (K)</th>
<th>$\Delta T^K_m / T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>506</td>
<td>141</td>
<td>0.279</td>
</tr>
<tr>
<td>Pb</td>
<td>601</td>
<td>175</td>
<td>0.291</td>
</tr>
<tr>
<td>Sb</td>
<td>903</td>
<td>173</td>
<td>0.192</td>
</tr>
<tr>
<td>Al</td>
<td>933</td>
<td>194</td>
<td>0.208</td>
</tr>
<tr>
<td>Ag</td>
<td>1234</td>
<td>221</td>
<td>0.179</td>
</tr>
<tr>
<td>Au</td>
<td>1336</td>
<td>246</td>
<td>0.184</td>
</tr>
<tr>
<td>Cu</td>
<td>1356</td>
<td>236</td>
<td>0.174</td>
</tr>
<tr>
<td>Mn</td>
<td>1493</td>
<td>264</td>
<td>0.177</td>
</tr>
<tr>
<td>Ni</td>
<td>1725</td>
<td>366</td>
<td>0.212</td>
</tr>
<tr>
<td>Co</td>
<td>1763</td>
<td>325</td>
<td>0.184</td>
</tr>
<tr>
<td>Fe</td>
<td>1803</td>
<td>382</td>
<td>0.212</td>
</tr>
<tr>
<td>Pd</td>
<td>1828</td>
<td>334</td>
<td>0.183</td>
</tr>
<tr>
<td>Pt</td>
<td>2043</td>
<td>377</td>
<td>0.185</td>
</tr>
</tbody>
</table>

homogeneous nucleation in the present paper is thus the lowest among the above various instability limits, at least for Al. In other words, with progressive superheating, a homogeneous nucleation catastrophe occurs before other catastrophes can intervene.

In fact, the effect of strain energy density ($\Delta E$) will be suppressed at higher temperatures if the temperature dependence of the elastic modulus for crystal is considered. Then the critical temperature for explosive homogeneous nucleation $T^K_m$ will be even lower. In an extreme case when $\Delta E$ tends to be zero, $T^K_m$ for Al was found to be only $1.13T_m$. If the effect of heterogeneous nucleation of melting at various defects is taken into account (such as those at dislocations, grain boundaries, or free interfaces), the critical superheating to activate nucleation catastrophe will be considerably depressed since the critical energy barrier and the critical nucleus size are smaller than those for the homogeneous one. In fact, the heterogeneous nucleation of melting at point defects inside the crystal, of which the equilibrium concentration increases at elevated temperatures, could not be avoided experimentally. The thermal distribution of defects may be effective in providing heterogeneous nucleation sites of the liquid phase, and hence reducing the stability limit. Therefore, the kinetic stability limit for superheated crystals in the present study in terms of the homogeneous nucleation catastrophe provides us with an upper bound of stability of the crystal lattice to which it can be, in principle, superheated.

It can also be seen from the above analysis that the critical temperature $T^K_m$ increases when the crystal size is smaller because a higher homogeneous nucleation rate (in a unit volume) is required. In other words, the kinetic stability limit is increasing with a decrease of the crystal dimension. This size effect of the kinetic stability limit may be responsible for some experimental observations that superheating increases with a decrease of the crystal size [15,16] when heterogeneous nucleation is avoided.

Melting of crystals should be a kinetic process for which the temperature-time-transformation ($T$-$T$-$T$) diagram can be constructed by means of the nucleation and growth rates. Suppose homogeneous nucleation with a constant rate ($I_{\text{hom}}$) and a polymorphous diffusion-controlled growth (with a constant rate of $U$) dominate the melting process, the volume fraction transformed at a given temperature ($T > T_m$) can be described as a function of time ($t$) [10]:

$$x = 1 - \exp\left(-\frac{\pi}{3} I_{\text{hom}} U^3 t^4\right).$$

FIG. 2. Time-temperature-transformation ($T$-$T$-$T$) curves for melting of a superheated crystal and for solidification of an undercooled liquid in aluminum. The volume fractions transformed are indicated by each curve. $T_\text{K}$ denotes the lower Kauzmann temperature, and $T'\text{m}$ the entropy catastrophe point, equivalent to an upper Kauzmann temperature.
Here the liquid phase is taken to be spherical and grows isotropically in three dimensions. The T-T-T curves for melting of the superheated crystal in Al are shown in Fig. 2, which differs fundamentally from those for solidification in the undercooled liquid. The melting T-T-T curves show a monotonic decrease of time when temperature rises, rather than a “C”-type curve as normally observed for solidification. This distinction originates from the different temperature dependence of the nucleation rates, as discussed above. The T-T-T curves for melting of the superheated crystals indicated that substantial superheating can be metastable in the experimental time scale providing no heterogeneous nucleation for melting is presented. Although the isentropic point (\(T_s^m\)) exists, as propose on the basis of the entropy catastrophe [7], it could be achieved only by applying an extremely high heating rate (greater than 10^{13} \text{ K/s} for a transformed volume fraction less than 10^{-6} from Fig. 2) to a crystal without any heterogeneous nucleation site. That does not seem to be feasible by using present-day heating techniques, therefore, the upper Kauzmann temperature will not be easily reached, at least for elemental metals in the present study. Even if such an ultrahigh heating rate could be realized, the life of the superheated crystal around \(T_s^m\) will be extremely short. Nevertheless, our result does not exclude the possibility of approaching the upper isentropic point in some materials such as solid solutions, compounds, ceramics, polymers, or even biological systems, if their kinetic critical points for homogeneous nucleation catastrophe are higher than the corresponding \(T_s^m\).

It is also anticipated from the present kinetic analysis that, for those low-dimensional materials (such as ultrafine particles or ultrathin films) whose size or thickness is smaller than the critical nucleus size \(r^*\), which is typically about 1 nm for metals), homogeneous nucleation of melting would become so difficult that \(T_s^m\) might be significantly elevated.

The authors are grateful for financial support from the National University of Singapore, where part of the work was performed, and from the National Science Foundation of China (Grant No. 58625101 and 59841004). Critical reading of the manuscript by Professor H. Jones and Professor R. W. Cahn is appreciated.

*Corresponding author. Electronic address: kelu@imr.ac.cn