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2000 J. Phys.: Condens. Matter 12 9123

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Heterogeneous nucleation catastrophe on dislocations in superheated crystals

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Received 11 May 2000, in final form 17 July 2000

Abstract. Heterogeneous nucleation of melt on dislocations in superheated crystals is analysed to give a superheating limit for massive heterogeneous nucleation on dislocations, which is evidently lower than the recently developed limit for homogeneous melting. Even for a crystal with a low dislocation density of 10^2 cm^{-2} of screw and edge unit dislocations, the associated threshold temperatures are only $1.068 T_m$ and $1.095 T_m$ respectively for various metals. It is also notable that the effect of dislocation density on this temperature is limited by the sharp decrease in the critical heterogeneous nucleation energy with increasing temperature.

Melting experiments of crystals have shown that if heterogeneous nucleation on the free surface can be avoided, crystals can be superheated [1–4]. Various superheating limits for crystals have been proposed, such as those defined by the entropy catastrophe [5], the volume catastrophe [6] and the rigidity catastrophe [7]. For example, Fetch and Johnson [5] have extended the Kauzmann paradox for glass transition [8] to superheated crystals, arguing that the crystal will melt at a critical temperature where the entropy of the superheated crystal equals that of the liquid phase. Thereby, they have established a thermodynamic limit of the isentropic temperature at $1.38 T_m$ for Al (where T_m is the equilibrium melting point) [5].

However, the actual amount of superheating with respect to the equilibrium melting point will be defined by kinetic considerations, even when the thermodynamic driving force is substantial [5, 9]. Recently, Lu and Li [9] proposed a new instability limit related to catastrophic homogeneous nucleation of melt in superheated crystals based on kinetic considerations. They have found [9] that a massive homogeneous nucleation catastrophe occurs in superheated crystals at a critical temperature of $1.2 T_m$, which is lower than the above instability limits [5–7]. This was based on the assumption that heterogeneous nucleation at grain boundaries, dislocations and free surfaces can be avoided. However, the superheating observed experimentally in metallic crystals is typically $1.10 T_m$, which is evidently still below this homogeneous kinetic limit [9, 10].

While heterogeneous nucleation on the surface and on grain boundaries can be avoided by appropriate surface coating [1–3] and by selecting of a single crystal respectively, heterogeneous nucleation on dislocations is not easy to eliminate. Even the most carefully annealed pure metals will have a dislocation density of 10^2 cm^{-2} or higher [11]. Early

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work by Glicksman and Vold [12] examined the case of heterophase dislocations. Later, from a thermodynamic point of view, Cotterill [13] suggested that melting could be based on dislocation multiplication. From a kinetic point of view, this paper is to describe the effects of heterogeneous nucleation of melt on dislocations and of the dislocation density on the superheating limit in superheated crystals in which heterogeneous nucleation on the free surface and on the grain boundaries are avoided. It is found that in a superheated crystal a massive heterogeneous nucleation catastrophe on dislocations occurs at a critical temperature T_m^H , which is lower than the recently established homogeneous instability limit T_m^K [9].

It has long been known that dislocations can act as heterogeneous sites for nucleation of precipitates in solids [11, 14]. Cahn [14] has proposed a model to estimate the effectiveness of a dislocation as a catalyst for nucleation of solid phases. Similarly, it is assumed here that a cylindrical liquid nucleus with a radius r , with cross-section perpendicular to the dislocation line, lies along the core of the dislocation, and that the matrix is an isotropic elastic substance. The energy change in forming this liquid cylinder consists of three terms, e.g. (a) a dislocation strain energy term, (b) a volume energy term including the free energy change and the strain energy due to volume change from solid to liquid and (c) a surface energy term. The dislocation strain energy term and volume energy terms favour nucleation whereas the surface energy term opposes it. The free energy change per unit length (ΔG_c) of forming a cylindrical liquid nucleus is then written as

$$\Delta G_c = -A \ln r + 2\pi\gamma r - \pi f r^2 + c \quad (1)$$

where $A = (\mu b^2/4\pi(1-\nu))$ for edge dislocations and $\mu b^2/4\pi$ for screw dislocations, c is a constant representing the non-elastic energy in the dislocation core, μ is the elastic shear modulus, b is the burger's vector, ν is the Poisson ratio; γ is the interfacial energy of the solid/liquid interface; $f = -(\Delta G_v + \Delta E)$ where $\Delta G_v = \Delta H_m(T_m - T)/T_m$ is the Gibbs free energy difference between the liquid and crystal (ΔH_m denotes the fusion enthalpy), and $\Delta E = 18E_y K \epsilon_0^2 f_0 / (4E_y + 3K)$, according to Allen *et al* [15], is the change in strain energy density resulting from the volume change upon melting where E_y is the Young's modulus and K is the bulk modulus for the solid, and f_0 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. ϵ_0 is the hydrostatic strain associated with the fractional volume change ($\Delta V/V$) during melting, i.e. $\epsilon_0 = \frac{1}{3}\Delta V/V$.

When the parameter $\alpha (= 2Af/\pi\gamma^2)$ is less than 1, a minimum in ΔG_c (equation (1)) exists at a value of r_0 , given by

$$r_0 = \frac{\gamma}{2f} \left[1 - \sqrt{1 - \frac{2Af}{\pi\gamma^2}} \right]. \quad (2)$$

This is interpreted as a sub-critical metastable cylinder of the liquid phase which initially surrounds the dislocation line. Such a cylinder with a radius of r_0 will be taken as the energetic starting point for nucleation. A local fluctuation which thickens the liquid phase requires energy. Beyond a certain size the volume energy will exceed the other terms and continued growth will result again in a lowering of energy. The maximum of the energy that must be supplied will depend on the shape and length of the nucleus along the dislocation where the fluctuation occurs. If we assume that the radius $r(z)$ of the liquid nucleus is a function of distance, z , along the dislocation line, the free energy, ΔG_h , for the formation of this liquid nucleus on the dislocation line is given by [14]

$$\Delta G_h(T) = \int_{-\infty}^{+\infty} \left[-A \ln \frac{r}{r_0} + 2\pi(r\sqrt{1+r'^2} - r_0) - \pi f(r^2 - r_0^2) \right] dz \quad (3)$$

where $r' = dr/dz$. The liquid nucleus is at a saddle point in $\Delta G_h(T)$, that is, its shape and size are determined by the conditions that ΔG_h is a minimum and a maximum in energy with respect to changes in shape and size respectively. Thereby, to determine the shape and size of the nucleus, the Euler–Lagrange equation [16] is applied to the integral in equation (3). Solving this equation yields values for $r(z)$ for which the integral is an extreme in $\Delta G_h(t)$ (either a maximum, minimum or saddle point), under the following boundary conditions that

$$\text{if } r = r_0 \quad r' = 0 \tag{4a}$$

$$\text{if } z = 0 \quad r' = 0. \tag{4b}$$

Letting $r/r_0 = 1 + y$, $z/r_0 = x$, $(1 - \alpha) = \beta^2$, the solution $r(z)$ can be written explicitly as

$$\frac{dy}{dx} = \sqrt{q^2 - 1} \tag{5}$$

where

$$q(y) = \frac{1 + y}{1 + [(1 + \beta)/2] \ln(1 + y) + \frac{1}{4}(1 - \beta)y(2 + y)}. \tag{6}$$

Substituting equation (5) into equation (3), the critical free energy change for nucleation of the liquid phase on a dislocation, $\Delta G_h^*(T)$, can be obtained as

$$\Delta G_h^*(T) = \frac{\pi \gamma^3}{f^2} (1 - \beta)^2 \int_0^\varepsilon (1 + y)(1 - q^{-2})^{1/2} dy \tag{7}$$

where the upper limit ε is determined by $q(\varepsilon) = 1$.

Figure 1(a) shows the temperature dependence of the critical free energy ΔG_h^* of formation of a liquid nucleus on a screw or an edge dislocation together with that for homogeneous nucleation of a spherical liquid nucleus for pure element Al. It shows that at low temperature, the critical energy of heterogeneous nucleation on a dislocation is close to that of the homogeneous nucleation. This is because when the critical energy is large the term due to the strain energy of the dislocation that favours nucleation on it is too small compared with that due to the volume free energy. However, as the temperature increases, the critical heterogeneous free energy drops sharply due to the assistance of dislocations.

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

$$I_D = I_0 \exp\left(-\frac{\Delta G_h^*(T)}{kT}\right) \exp\left(-\frac{Q}{kT}\right) \tag{8}$$

where Q is the activation energy for atomic diffusion in the crystal lattice, and I_0 is a prefactor which can be approximated by $I_0 = n^{1/3}L(kT/h)$ [14], where n is the number of atoms in a unit volume, L is the dislocation line length per unit volume, k is Boltzmann's constant and h is Planck's constant. Figure 1(b) shows the calculated results of nucleation rate of melting on dislocations as a function of temperature in pure Al, compared with that of the nucleation rate of homogeneous melting for a perfect aluminium crystal. The result shows that the critical superheating temperatures required to give one nucleus per second per cm^3 under the conditions of heterogeneous nucleation of melting on dislocations in Al with a dislocation density of 10^2 cm^{-2} were 1027 K and 1044 K for unit screw and edge dislocations respectively, compared with 1127 K obtained for homogeneous nucleation [9], corresponding to a drop from 1.208 to 1.101 and 1.119 T_m for Al. On the other hand the calculation of nucleation rate in equation (8) did not consider the effect of the presence of dislocations on the diffusion process, which will change the diffusion in the solid [17]. However, there is no doubt that equation (8)

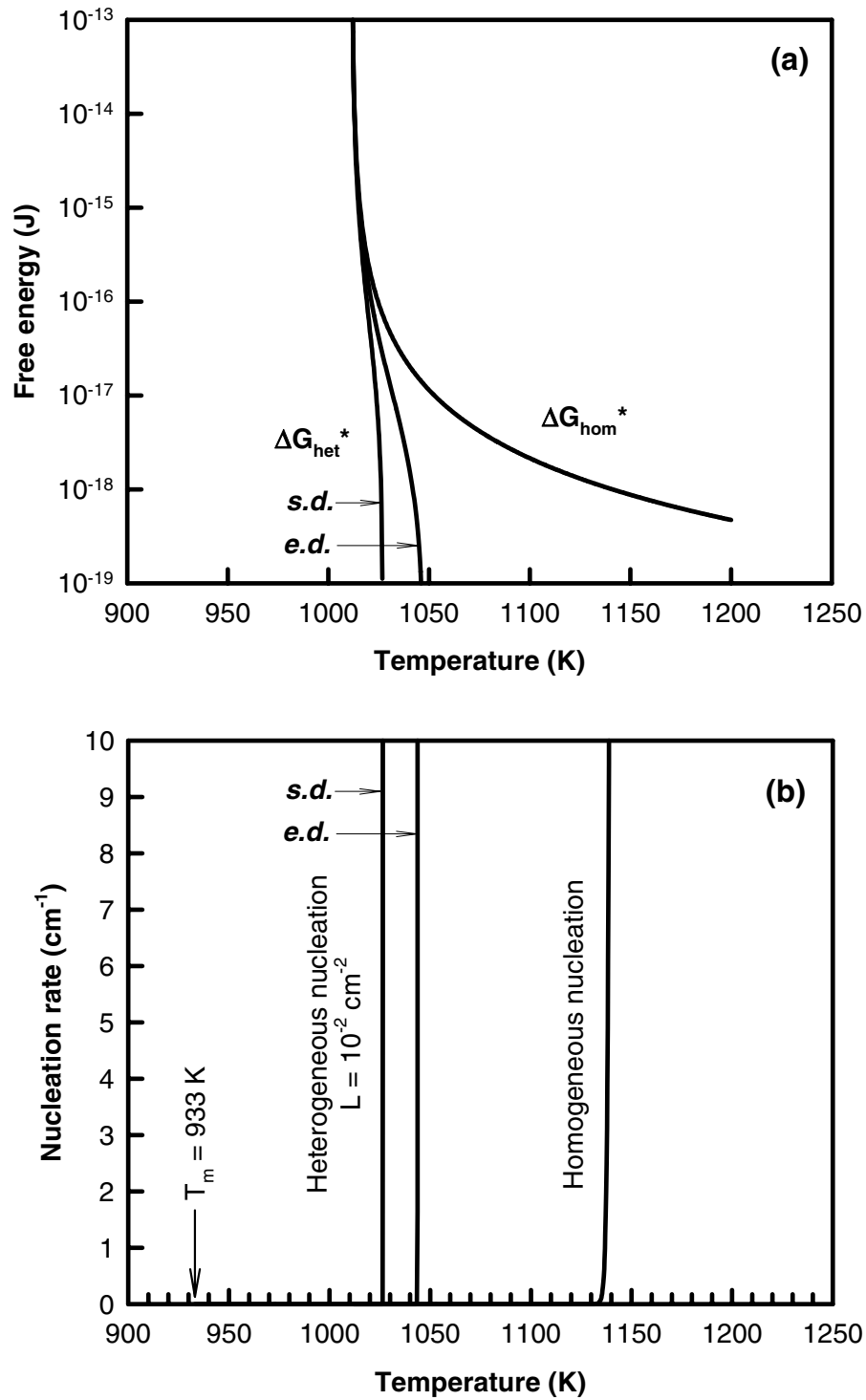


Figure 1. (a) Critical free energy change for nucleation of melting, homogeneously and heterogeneously on screw or edge dislocations as a function of temperature for pure aluminium; (b) rate of homogeneous and heterogeneous on screw and edge dislocations for melting of a superheated Al crystal. (S.d. and e.d. denote screw dislocation and edge dislocation respectively.)

Table 1. Results of calculated absolute and relative critical superheating required to give one nucleus per second per cm^3 for homogeneous and heterogeneous nucleation of melting in various metals.

Metal	Structure	T_m (K)	T_m^K (K)	$T_m^{H(\alpha=1)}$ (K)	Dislocation density L (cm^{-2})					
					$L = 10^2$		$L = 10^6$		$L = 10^{10}$	
					T_m^H	ΔT_r	T_m^H	ΔT_r	T_m^H	ΔT_r
Pb	f.c.c.	601	776	699	685	0.140	683	0.136	681	0.133
Al	f.c.c.	933	1127	1047	1044	0.119	1043	0.118	1042.6	0.117
Ag	f.c.c.	1234	1455	1329	1324	0.073	1323	0.072	1322	0.071
Cu	f.c.c.	1356	1592	1461	1455	0.073	1454	0.072	1453	0.072
Ni	f.c.c.	1725	2091	1887	1878	0.089	1876	0.088	1874	0.086
Fe	b.c.c.	1809	2191	1982	1962	0.085	1959	0.083	1957	0.082
Zn	h.c.p.	693	905	774	772	0.114	771.4	0.113	771	0.113
Mg	h.c.p.	922	1087	991	987	0.07	986	0.069	985	0.068

Note: $\Delta T_r = \Delta T_m^H / T_m$.

will give us a good estimation on nucleation rate since the dominant effect of dislocation is in reducing the critical nucleation energy, rather than in modifying the diffusion process.

The calculated critical superheating limits of several typical elemental metals due to heterogeneous nucleation on dislocations with densities of 10^2 and 10^{10} cm^{-2} are listed in table 1. The Burgers vectors, \vec{b} of a unit dislocation are $(a_0/2)\langle 110 \rangle$, $(a_0/2)\langle 111 \rangle$ and $(a_0/2)\langle 11\bar{2}0 \rangle$ [18] for fcc, bcc and hcp crystals respectively, where a_0 is the lattice constant. Unit dislocation is used because it has the highest dislocation strain energy compared with partial dislocation in real crystal, which will give lower superheating limits. Table 1 shows that for the elements listed in the table the relative critical superheating ΔT_r ($= (T_m^H - T_m) / T_m$) for heterogeneous nucleation on unit screw and edge dislocation are found to be around $0.068(\pm 0.023) T_m$ and $0.095(\pm 0.026) T_m$ respectively, less than half of the relative superheating obtained for the homogeneous nucleation limit in the similar group of elements [9]. This result is lower than previously established superheating limits and is consistent with the superheating observed experimentally in metallic crystals, typically $1.10 T_m$ [9].

Our results in table 1 also show that the dislocation density, L , has little effect on superheating limit. For example, it was found that the superheating of Pb decreased by 4 K from 685 K for an edge dislocation density of 10^2 cm^{-2} to 681 K with a dislocation density of 10^{10} cm^{-2} . One of the explanations from equation (8) is that the critical heterogeneous nucleation rate is determined by the prefactor and the critical nucleation energy in the exponential term. Since the latter drops sharply with slight increase in temperature (figure 1(a)), the exponential term containing the critical nucleation energy is effectively the dominant factor and the increase in dislocation density is more than compensated for by the decrease in the energy term. This indicates that the effect of dislocations on melting is mainly in reducing the activation energy for nucleation and the dislocation density has little effect on the melting temperature.

From equations (1) and (2), if α ($= 2Af/\pi\gamma^2$) is larger than 1, it is evident that there will be no energy barrier for the formation of a cylindrical liquid nucleus around a dislocation, which indicates that the sum of the first two terms in equation (1) increases more rapidly than the surface energy term. A critical superheating limit $T_m^{H(\alpha=1)}$ for this condition can be calculated when $\alpha = 1$. The result in fact is the ultimate limit for heterogeneous nucleation of melting on dislocations, since, above this temperature, dislocations are so effective that there

will be no energy barrier for nucleation of liquid on them, just as for the free surface. However, from table 1 it is seen that the values of $T_m^{H(\alpha=1)}$ for the selected elements are very close to T_m^H , which gives only a slight increase of between 1 and 20 K.

It should be noted that the assumption made in the present model that the liquid nucleus initially nucleates along the cores of dislocations is supported by the molecular dynamics simulation work by Huang *et al* [19]. Their results showed that the nucleation barrier for the liquid is much smaller near the dislocation cores than in the bulk and melting is initiated systematically in the region near the cores for their studied system (copper). In conclusion, we have analysed the heterogeneous nucleation of melt on dislocations in superheated crystals. A stability limit for massive heterogeneous nucleation on dislocations is found to be lower than the recently developed limit for homogeneous melting. Even for a crystal with a low dislocation density of 10^2 cm^{-2} , the associated threshold temperatures are only 1.068 and 1.095 T_m for screw and edge dislocations respectively in various metals. It is also notable that the effect of dislocation density on this temperature is limited by the sharp decrease in the critical heterogeneous nucleation energy with increasing temperature.

Acknowledgment

The authors are grateful for the critical reading of the manuscript by Professor H Jones.

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