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Kinetic stages in the crystallization of deeply undercooled body-centered-cubic and face-centered-cubic metals

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Abstract

Crystallization velocities in several face-centered-cubic (fcc) and body-centered-cubic (bcc) metals are calculated using molecular dynamics computer simulations for the (1 0 0) and densely packed (1 1 1) or (1 1 0) planar interfaces. We show that the crystallization kinetics can be divided into high- and low-temperature regimes, separated at a crossover temperature, T_c, which is associated with kinetic arrest. In the high-temperature regime, the velocity in both fcc and bcc metals initially increases with the degree of undercooling before reaching a maximum somewhat above the glass temperature. The kinetics is characterized by a thermally activated process. In the low-temperature regime, stresses develop in the interface and reduce the apparent activation energies for interface mobility. For the fcc metals (Cu, Ni, Ag and Pt) the activation energies fall essentially to zero, indicating an athermal process. For bcc metals (Fe, Mo, V, Ta) the activation energies remain finite, varying from ≈0.013 eV (Ta) to ≈0.2 eV (Mo).

Keywords: Crystallization; Interface dynamics; Kinetics; Molecular dynamics; Metals

1. Introduction

Solidification has long been a topic of both scientific [1] and practical interest [2], owing to its fundamental importance in the processing of metal alloys [3–5]. In recent years, this interest has been further motivated by the potential to fabricate more advanced materials such as bulk metallic glasses and nanocrystalline materials. Despite these many years of investigation, basic questions concerning the rates and mechanisms of atom transfer from the liquid to the solid remain unanswered, even in the simplest metals [4]. These questions, however, can now be practically addressed using large-scale molecular dynamics simulations and other modeling methods [4], and indeed, several such studies have now been carried out [6]. Most studies to date have focused on solidification near the melting point, T_m, where equilibrium concepts can be applied [4,6]. In the present work, we also use molecular dynamics to investigate crystallization in pure metals, but here we focus on temperatures far below T_m and even below the glass temperature, T_g. As we will show, this deeply undercooled region provides understanding of the crystallization process not easily gained from studies carried out at higher temperatures.

For solidification near T_m, the interface mobility is often characterized by a kinetic coefficient, μ, which is the constant of proportionality between the growth velocity (V) and undercooling ($\Delta T \equiv T_m - T$), i.e., $V = \mu \Delta T$. The kinetic coefficient, μ, is defined through $\mu \equiv \frac{\partial V}{\partial T}\big|_{T=T_m}$, and is usually approximated using

$$\mu = C \frac{V_T L}{k_B T_m^2} \tag{1}$$

where L is the latent heat, and $V_T = \sqrt{3k_B T/M}$ with M the atomic mass. The kinetic coefficient is useful as it characterizes the behavior of the front close to the melting tempera-

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ture where the temperature dependence of the velocity is predominantly controlled by the difference in free energies of the crystalline and liquid phases. Values of C in pure metals are in the range 0.8–1.4 for the (1 0 0) interface [7,4]. In this high-temperature regime, it has been shown that the velocity is different on different crystallographic planes, and that this orientation dependence is related to kinetic factors, and not to an anisotropy in the free energy [4,8]. These findings regarding the anisotropy of μ were obtained in face-centered-cubic (fcc) [9], body-centered-cubic (bcc) Fe [10] and hexagonal-close-packed (hcp) Mg [11] metals and can be roughly explained within the framework of Mikheev–Chernov kinetic density functional theory [12,4]. As noted, much less work has been carried out at lower temperatures. This is perhaps due to the experimental difficulty in supercooling pure metals below $T \approx 0.85T_m$, although a recent study on the solidification rates in Ag has been reported at temperatures as low as $T = 0.6T_m$, which is ≈150 K above its calculated value of T_g [13].

The solidification kinetics far from the melting temperature differ from that near T_m in that the temperature dependences of the thermodynamic driving forces and atomic mobilities are very different at T_m than at T_g. At the higher temperatures the thermodynamic driving force for crystallization is very sensitive to temperature, but the atomic mobility is not. At T_g, just the opposite situation exists. This can be realized by examining the two basic models of solidification: one based on transition rate theory and the other on a collision-limited theory. The former predicts that the velocity of the crystallization front is controlled by diffusion and is given by a Wilson–Frenkel type expression [14],

$$V(T) = C\exp(-Q/k_BT)[1 - \exp(-\Delta G(T)/k_BT)] \quad (2)$$

where ΔG is the difference in free energy between the melt and crystal, and Q is the activation energy for diffusion. While this approach appears to work well in MD simulations of Si [15], Broughton et al. (BGJ) [16] have shown using a Lennard–Jones potential (which they assume to be metal-like), that their data are fit far better by the expression

$$V(T) = C\sqrt{T}[1 - \exp(-\Delta G(T)/k_BT)] \quad (3)$$

The prefactor, C, is usually interpreted as $C = \frac{a}{\lambda}\sqrt{\frac{3k}{m}}f$, where a is the interatomic spacing, $\lambda < a$ the displacement during crystallization and f a constant of the order of unity. This latter expression derives from the assumption of collision-limited kinetics, as first suggested by Turnbull [1], and thus the maximum crystallization velocity is controlled by the average thermal velocity, $v = \sqrt{3kT/m}$ of atoms in the melt. Note that Eq. (1) represents the first term in the expansion of Eq. (3) near T_m. Similar results were published for simulations using EAM type potentials of transition metals [6], although deviations from Eq. (3) were noted as ΔT increased beyond $\Delta T/T_m \approx 10$ [6]. In this paper we measure crystallization velocities at temperatures down to $0.1T_m$ for a variety of fcc and bcc metals and offer an interpretation that can explain the observed behavior in all of these metals within a single framework.

2. Numerical procedure

2.1. Interatomic potentials

MD simulations were performed using a variety of many-body embedded atom method (EAM) potentials. In all cases, care was taken to choose potentials that were shown to reproduce equilibrium as well as non-equilibrium properties. As we will show in Section 3, we interpret some of the results in terms of thermally activated processes, and therefore seek potentials that are proven to reproduce melting temperatures, defect configurations, and defect migration energies. Rather than discuss the specific properties of each potential, we simply list in Table 1 the reference for each potential and the corresponding values of T_m and T_g that we determined. We mention, however, that for Fe we used the EAM parameterization presented in Ref. [17], which was obtained by fitting both melting and defect properties. This potential does not predict correctly solid structural phase transitions; for the present work, however, this deficiency, in fact, simplifies the interpretation. The melting temperatures reported here were found by interpolating the velocities versus temperature data to zero velocity. Glass temperatures were calculated according to the definition of the calorimetric glass temperature, i.e., the crossing of a linear extrapolation of the enthalpy versus temperature of the supercooled liquid and the glassy states [18]. This procedure was repeated for various cooling rates ranging from 10^{11} K s^{-1} to 10^{15} K s^{-1}. Although these rates are unrealistic experimentally, glass temperatures found using these rates should represent well kinetic arrest within the framework of the simulation where relevant response times are of the order of $\tau \approx 10^{-12}$ s [32].

2.2. Measuring crystallization velocities

In order to calculate the crystallization velocity we first created a sample composed of a relaxed liquid and a relaxed solid with identical cross-sectional dimensions, ≈20 × 20 nm^2. The two periodic systems were joined along the Z direction and then relaxed together at the melting temperature for 100 ps. The total length of the system was approximately 60 nm and contained ≈5 × 10^5 atoms. The relaxed system was subsequently quenched to different target temperatures. Quenching was performed by applying a Berendsen thermostat to the whole system [25]. The lateral size was fixed to the theoretical crystalline size according to the thermal expansion coefficient; the pressure along the Z direction was controlled to accommodate the change in volume of the cell. The measured velocities were not sensitive to the details of this procedure, since velocities were measured only after a steady interface velocity had been achieved. In addition, for most systems we report