JOURNAL OF CHEMICAL PHYSICS VOLUME 117, NUMBER 23 15 DECEMBER 2002

Effects of nucleation transience on crystallization kinetics under strongly nonequilibrium conditions

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(Received 28 May 2002; accepted 17 September 2002)

An approach to quantitatively assess the effects of nucleation transience on the kinetics of crystallization under static and dynamic conditions is proposed. The approach is based on an order of magnitude analysis that involves time scales characterizing the rates of nucleation relaxation and processing. The method is implemented to evaluate the effects of nucleation transience on kinetic computations performed in the tungsten–carbon system. The assessment is verified by contrasting the kinetics computed by means of a cluster dynamics simulation that implicitly accounts for transience to those evaluated using a quasi-steady-state model. When interpreting the kinetics of tungsten carbide surface crystallization, the proposed scaling method predicts that under static conditions transient effects need to be accounted for when annealing below 2600 K, while under dynamic conditions transient effects become important when quenching at ultrahigh cooling rates such as 10^8 K/s. Accordingly, in the case of isothermal annealing the steady-state kinetics appears to be in good agreement with those computed dynamically above 2600 K, but gradually deviates at lower temperatures. Consequently, the steady-state model underestimates the transformation time by more than an order of magnitude at the nose of the TTT curve ($\sim$2200 K). In the case of continuous cooling, the kinetic rate is well approximated by the quasi-steady-state model for processing rates of 10^4 and 10^6 K/s; however, for ultrahigh cooling rates of order 10^8 K/s, the kinetics computed by the quasistatic model deviates substantially from that computed using cluster dynamics. As a consequence, the crystallized fraction computed from the quasistatic model is overestimated by at least an order of magnitude at every undercooling temperature. The results from the two kinetic models appear to validate the assessment of transience based on the proposed scaling method. [DOI: 10.1063/1.1519837]

I. INTRODUCTION

Nucleation, which is the initial stage of phase transition, often has a tremendous effect on subsequent microstructural transitions that occur beyond that stage, as the kinetics of nucleation often controls the selection of the dominant kinetic path and therefore determines phase selection and consequently microstructural evolution.[1] In condensed systems, nucleation starts with the stochastic creation of crystal-like embryos, leading to spontaneous formation of small, unstable clusters of the new crystalline phase. Many of these clusters dissolve, as their probability to decay is greater than to grow, others eventually grow to a critical size beyond which their probability to grow is greater than to decay, and eventually develop into stable nuclei. Crystallization then proceeds by deterministic growth of these nuclei up to sizes beyond which the interfacial barriers vanish and the kinetics becomes transport limited. The transformation then advances by transport-limited evolution of microstructural morphologies.

Under static conditions, a steady state characterized by a constant rate of formation of stable nuclei is established. The time during which a cluster hierarchy is evolving to facilitate continuous formation of stable nuclei is referred to as the transient period. Under highly nonequilibrium processing conditions realized in processes such as thermal spraying or laser cladding, transient times could be rather long and often detectable. When interpreting crystallization kinetics under such processing conditions, it may appear necessary to account for such transient behavior as its disregard may contribute to severely overestimating the kinetic rate. Hence, quantifying the extent to which nucleation transience affects the kinetic rate is of vital interest when modeling crystallization kinetics, as it facilitates in assessing the dynamics of the transition.

In early kinetic analyses of nucleation-controlled processes, transience was ignored and nucleation was treated as a steady or quasisteady process. More recently, several authors[2,3] have attempted to account for transience by employing the analytical expression for the transient nucleation frequency under static conditions derived by Kashchiev,[4] and have demonstrated to a certain extent the effect of transience on the kinetics of nucleation. Several other authors, however,[5–7] have attempted to simulate nonisothermal conditions by integrating that same expression over temperature. Kelton and Greer[8] argued that such treatment is clearly unjustified, as it implicitly assumes that the nucleation frequency at any instant is as it would have been after annealing at the instantaneous temperature for the elapsed time since

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the beginning of the quench. In general, the assumption that any expression for the isothermal case can be extended to simulate nonisothermal behavior is fundamentally flawed since transient periods at different annealing temperatures do not necessarily coincide with those under continuous temperature change at the corresponding instantaneous temperatures. Corrections to the quasisteady approximation for transient effects were proposed by Granasy, who developed an iterative methodology that utilizes parameters from cluster dynamics calculations,[9] and by Shneidman, who employed asymptotic (singular perturbation) techniques.[10]

In this study, an approach to quantitatively assess the extent to which nucleation transience may affect the prediction of crystallization kinetics under strongly nonequilibrium conditions is presented. The proposed approach is implemented to assess the effects of transience in kinetic predictions performed in the tungsten–carbon system. The assessment of transience is achieved by a simple scaling analysis involving internal and external time scales that characterize the rates of nucleation relaxation and processing, respectively. In order to validate the proposed methodology, the crystallization kinetics is evaluated by means of a stochastic computational model which involves numerical integration of cluster dynamics equations established from rate theory and thus implicitly accounts for transience, as well as by a quasistatic model which is based on time integration of the steady-state nucleation rate and therefore neglects transience. Contrasting the dynamically computed kinetics to those evaluated by assuming quasistatic conditions hence validates the assessment of transience based on the proposed scaling analysis.

II. CLASSICAL THEORY OF ATOMIC CLUSTERING

In the context of the classical theory of nucleation in condensed systems, fluctuation in the formation of an n-size cluster of surface area A_n is associated with the excess Gibbs energy needed for its formation ΔG_n, and can be expressed as the balance between volume and surface contributions as follows:

$$\Delta G_n = -n\Delta\mu + A_n\sigma, \tag{1}$$

where $\Delta\mu$ and σ are the macroscopic (independent of n) thermodynamic supersaturation and interfacial energy, respectively.[11] A maximum in ΔG_n, denoted as ΔG_{n*}, is obtained at a critical size $n*$ and is referred to as the critical activation energy.

According to the rate theory of atomic clustering, nucleation can be modeled by a set of discrete attachment–detachment kinetic equations that has the form of a master equation

$$\begin{aligned}\frac{dN_n(t)}{dt} &= I_{n-1}(t) - I_n(t)\\ &= N_{n-1}(t)k_{n-1}^{+} - [N_n(t)k_n^{-} + N_n(t)k_n^{+}]\\ &\quad + N_{n+1}(t)k_{n+1}^{-},\end{aligned} \tag{2}$$

where $N_n(t)$ and $I_n(t)$ are the time-dependent density and nucleation frequency at size n, respectively. Stochastic evolution theory dictates that under static conditions (e.g., under constant temperature) a steady-state cluster distribution would be established such that the nucleation frequency becomes constant. In the Turnbull–Fisher model, the rate of monomer attachment and detachment to an n-size cluster, k_n^{+} and k_n^{-}, is given by

$$k_n^{+} = O_n\gamma \exp\left(-\frac{\Delta G_{n+1} - \Delta G_n}{2k_BT}\right), \tag{3a}$$

$$k_{n+1}^{-} = O_n\gamma \exp\left(-\frac{\Delta G_n - \Delta G_{n+1}}{2k_BT}\right), \tag{3b}$$

where O_n is the number of interfacial atomic sites, γ is the unbiased molecular jump frequency, and k_B is the Boltzmann's constant. The evolution of cluster size distribution and the nucleation frequencies can be obtained by solving the system of stiff, coupled differential equations given by Eq. (2). This can be accomplished by means of a stiff ODE solver that is supplied with the rate constants and with appropriate boundary and initial conditions.[11,12]

The time-dependent extended volume crystallized fraction, $x_e(t)$, can be established by accounting for the volume of all supercritical clusters, i.e.,

$$x_e(t) = V_m \sum_{n \geqslant n*} nN_n(t),$$

where V_m is the molecular volume. For clusters sufficiently exceeding the critical size, however, the diffusion component of the nucleation rate characterizing size fluctuations becomes vanishingly small in relation to the drift component that accounts for deterministic growth. Hence, ignoring fluctuational growth for $n \gg n*$, a growth law may be derived as $dn/dt \cong I_n(t)/N_n(t)$, where dn/dt is the drift velocity or post-nucleation growth rate. Taking n to be continuous and assuming a transition from fluctuational to deterministic growth at a postcritical size $n_{\text{post}} \gg n*$, the growth law may be employed to yield a time-integral form of $x_e(t)$ as[12]

$$x_e(t) = V_m \int_0^t n(t;t')I_{n_{\text{post}}}(t')\,dt'. \tag{4}$$

The convolution function $n(t;t')$ denotes the size of a supercritical cluster at time t which nucleated at a time t' when $n(t';t') = n_{\text{post}}$. It can be obtained by solving the initial value problem governing the time evolution of a supercritical cluster

$$\begin{aligned}\frac{dn}{dt} &\equiv k_n^{+} - k_n^{-} \approx k_n^{+} - k_{n+1}^{-}\\ &= 2O_n\gamma \sinh\left\{\frac{\Delta\mu}{2k_BT}\left[1 - \left(\frac{n*}{n}\right)^{1/3}\right]\right\}.\end{aligned} \tag{5}$$

In the case of surface crystallization, V_m and $n(t;t')$ in Eq. (4) appear to the 2/3 power as dictated by the dimensionality of a catalyzed transition.[12] The time-dependent volume crystallized fraction that accounts for the overlap of crystallites, $x(t)$, can be obtained from the Avrami statistical model[13] as $x(t) = 1 - \exp[-x_e(t)]$. The cluster dynamics simulation is discussed in detail in the work of Demetriou *et al.*[1]

III. STEADY-STATE APPROXIMATION

In the limit of n being continuous, a closed-form expression for the steady-state nucleation frequency in the vicinity of the critical size can be obtained as

$$I^s = z k_{n*}^{+} N_{n*}^{e}, \tag{6}$$

where N_{n*}^{e} is the equilibrium cluster size distribution taken as a Boltzmann distribution function, and $z = [(-d^2 \Delta G_n / dn^2)_{n=n*} / 2\pi k_B T]^{1/2}$ is the Zeldovich factor. Furthermore, in the limit of n being continuous, the induction time for the nucleation of critical clusters, ϑ_{n*}, which may be regarded as the nucleation relaxation time, has been derived analytically as[4]

$$\vartheta_{n*} = \frac{2}{3\pi k_{n*}^{+} z^2}. \tag{7}$$

Taking the nucleation rate relaxed at its steady-state value throughout the transformation time and under the assumption of zero-size nuclei and infinitely large crystals, a quasistatic analog of Eq. (4) may be obtained as

$$x_e(t) = \frac{4}{3}\pi \int_0^t \left\{ \int_{t'}^{t} u(t'')dt'' \right\}^3 I^s(t')dt', \tag{8}$$

where u is the size-independent crystal growth velocity given as $u = [(dr/dn)(dn/dt)]_{r\to\infty}$. Under static conditions the kinetics can be further reduced to

$$x_e(t) = \frac{\pi}{3} I^s u^3 t^4. \tag{9}$$

For surface nucleation, the term $\frac{4}{3}$ in Eq. (8) becomes 1, the growth rate exponent in Eqs. (8) and (9) becomes 2, and the time exponent in Eq. (9) becomes 3.[12]

IV. TRANSIENT EFFECTS DURING STATIC PROCESSING

Under static conditions realized upon isothermal annealing, the effects of nucleation transience become significant when the transformation time τ, which can be computed from Eq. (9) for a given crystallized surface fraction, becomes comparable to the relaxation time ϑ_{n*}. Hence, a criterion for the validity of the steady-state approximation can be formulated based on time-scale analysis as follows:

$$\tau \gg \vartheta_{n*}. \tag{10}$$

The induction time along with the transformation time for 1-ppm (10^{-6}) surface crystallization of tungsten carbide were computed from Eqs. (7) and (9), respectively, based on the thermodynamic and kinetic data employed by Demetriou *et al.*,[1] and are plotted in Fig. 1 against temperature. The induction time ϑ_{n*} appears to be excessively large near equilibrium and near glass transition owing to a diminished driving force and atomic mobility, respectively, while it attains a minimum at intermediate temperatures where both supersaturation and atomic mobility remain moderate. The transformation time τ appears to be much longer than ϑ_{n*} at temperatures above 2600 K, implying that transient effects upon isothermal annealing above 2600 K can be neglected. At lower temperatures however, the transformation time lags the induction time by up to two orders of magnitude. Hence, transient effects upon annealing below 2600 K are anticipated to be significant. Accordingly, a steady-state kinetic model that neglects transience would successfully model the kinetics above 2600 K but it is expected to fail at lower temperatures, as the kinetic rate would be severely overestimated.

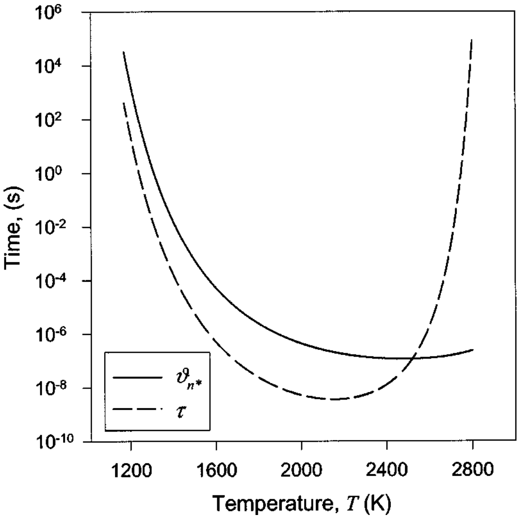

FIG. 1. Induction and isothermal transformation times for tungsten carbide surface crystallization at different temperatures.

In order to illustrate the effects of transience on the kinetics of nucleation during isothermal annealing, the nucleation frequency computed from cluster dynamics at 2600 K is considered. The induction time at 2600 K is evaluated from Eq. (7) to be 0.125 μs. The annealing duration is taken to be 1.5 μs, about an order of magnitude greater than ϑ_{n*}. The time-dependent nucleation frequencies at $n*$ and n_{post} $\times(\approx 1.5n*)$ are computed from Eq. (2) and are plotted in Fig. 2, along with the steady-state nucleation rate evaluated from Eq. (6). The nucleation frequency at the critical size appears to attain its steady-state value at $\sim 3\vartheta_{n*}$, in

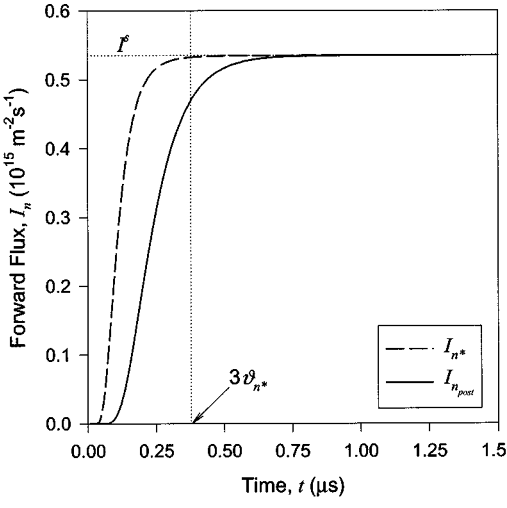

FIG. 2. Surface nucleation frequency of tungsten carbide vs time during annealing at 2600 K for 1.5 μs.

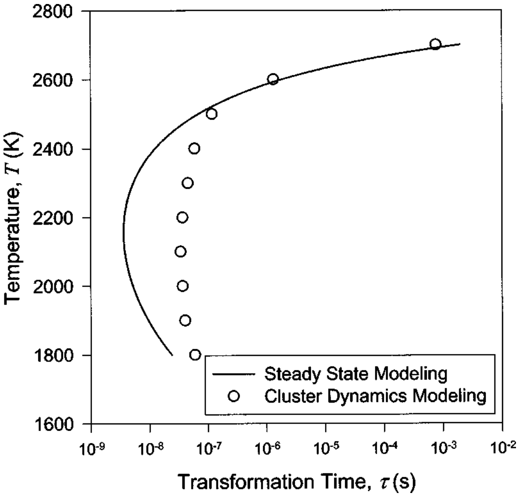

FIG. 3. Transient and steady-state TTT diagrams for 1-ppm tungsten carbide surface crystallization.

accordance with the analytical treatment of Kashchiev,[4] while the nucleation frequency at the postcritical size attains its steady-state value at $\sim 6\vartheta_{n*}$ (i.e., at ~60% of τ).

In order to demonstrate the effects of nucleation transience on the kinetics of crystallization at different annealing temperatures and hence justify the assessment based on Eq. (10), the isothermal transformation diagram (TTT curve) for this transition is computed from cluster dynamics and is contrasted to the one obtained using the steady-state model. The transient and steady-state TTT diagrams are shown in Fig. 3. The gradual deviation in the computed transformation time obtained from the two models, which becomes apparent at 2600 K and reaches more than an order of magnitude at the nose of the TTT curve, is clearly illustrated. The isothermal-transformation diagram in Fig. 3 demonstrates quantitatively the importance of nucleation transience in computing isothermal kinetics under deep undercoolings. Moreover, it verifies that transience can be accurately assessed by means of a simple time-scale analysis as given in Eq. (10).

V. TRANSIENT EFFECTS UNDER DYNAMIC PROCESSING

Under dynamic conditions realized upon continuous cooling, transient effects attributed to the explicit dependence of the activation barriers on temperature may become significant when the barriers change faster than the rate at which nucleation relaxes. Schneidman[10] suggested that the barrier rate of change that limits transience during dynamic processing appears to be that of nucleation, i.e., $d\Delta G_{n*}/dt$. A time scale to characterize the rate of change of the nucleation barrier may be defined as follows:

$$\varphi_{n*} \equiv \left[\frac{d}{dt} \left(-\frac{\Delta G_{n*}}{k_B T} \right) \right]^{-1}. \tag{11}$$

Owing to the temperature dependence of the activation barrier, φ_{n*} becomes inversely proportional to the processing rate dT/dt. Hence, comparing this dynamic time scale to the nucleation relaxation time could provide an indication of the importance of transient effects during dynamic processing. A criterion for the validity of the quasi-steady-state approximation can therefore be formulated as follows:

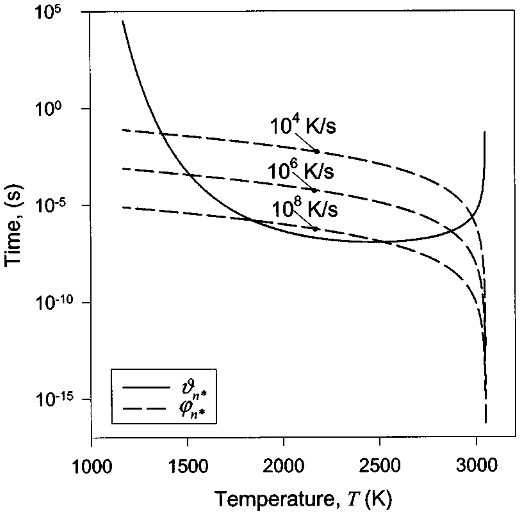

FIG. 4. Relaxation time and time scales characterizing the barrier rate of change under various cooling rates for tungsten carbide surface crystallization.

$$\varphi_{n*} \ll \vartheta_{n*}. \tag{12}$$

The time scales that characterize the barrier rate of change for tungsten carbide surface nucleation for 10^4, 10^6, and 10^8 K/s cooling rates were computed from Eq. (12) based on the thermodynamic and kinetic data employed by Demetriou *et al.*,[1] and are plotted against temperature in Fig. 4 along with the relaxation time ϑ_{n*}. Figure 4 suggests that φ_{n*} increases monotonically along the cooling process in a fashion that resembles the monotonic decrease of nucleation barrier with temperature. Furthermore, the equally displaced "isocooling-rate" curves signify the inverse proportionality between φ_{n*} and dT/dt. According to the scaling criterion given by Eq. (12), for moderate-to-high cooling rates ($10^4 - 10^6$ K/s) transient effects may become considerable only when the transformation initiates near equilibrium or concludes near glass transition, while for ultrahigh cooling rates (10^8 K/s) the effects of transience may dynamically dominate the entire crystallization process.

In order to illustrate the effects of transience on the kinetics of nucleation during continuous cooling, the transient nucleation frequency of postcritical clusters computed by means of cluster dynamics for different cooling rates is plotted against temperature in Fig. 5 within the corresponding transformation range. To accentuate transience, the temperature-dependent quasi-steady-state rate is also plotted in Fig. 5. For the processing rates of 10^4 and 10^6 K/s, the transient nucleation frequency appears indistinguishable from the quasi-steady-state rate as the transitions take place between 2800 and 2500 K where the rate at which nucleation relaxes is greater than the rate at which the nucleation barrier changes. For 10^8 K/s however, the transient nucleation frequency deviates substantially from the quasi-steady-state rate, as nucleation remains transient throughout the transition.

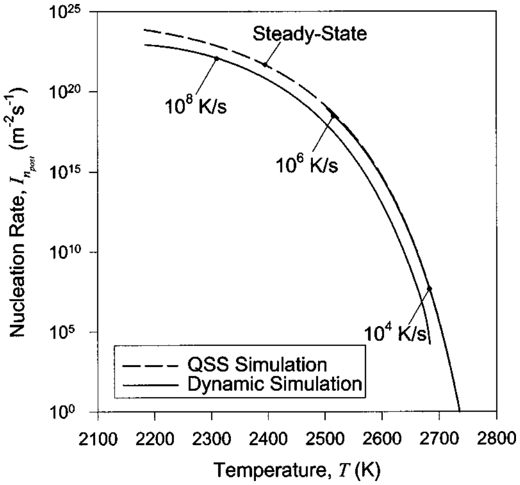

FIG. 5. Surface nucleation frequency of tungsten carbide vs temperature during continuous cooling for various cooling rates.

In order to illustrate the effects of transience on the kinetics of crystallization during continuous cooling, the kinetics computed from the dynamic simulation for 10^4, 10^6, and 10^8 K/s cooling rates is plotted in Fig. 6 against temperature along with that computed from the QSS simulation. In accordance with Figs. 4 and 5, transient effects appear insignificant for processing under 10^4 and10^6 K/s cooling rates, while for 10^8 K/s the dynamically evaluated kinetics deviates substantially from the quasistatic ones, as the crystallized fraction is overestimated by at least an order of magnitude at every undercooling temperature. The continuous-cooling transformation diagram in Fig. 6 demonstrates quantitatively the significance of transience during quenching at high cooling rates, and verifies that transience can be accurately predicted by means of a time scale analysis as given by Eq. (12).

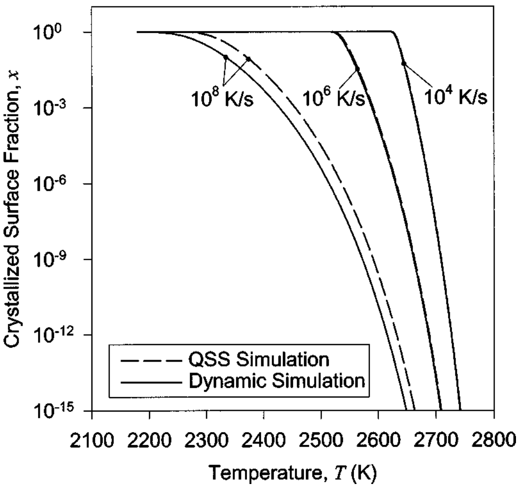

FIG. 6. Surface crystallization of tungsten carbide vs temperature during continuous cooling for various cooling rates.

VI. CONCLUSIONS

Rigorous interpretation of nucleation-controlled kinetics under highly nonequilibrium processing conditions often requires consideration of the transient nucleation behavior. In this study, methodologies to quantitatively assess the importance of transient effects in interpreting the kinetics of crystallization under static (isothermal) and dynamic (nonisothermal) conditions are proposed based on time-scale analyses. The proposed methodologies are implemented to quantify transience during surface crystallization of tungsten carbide.

Under static conditions realized upon isothermal annealing, the effects of nucleation transience become significant when the transformation time becomes comparable to the nucleation relaxation time. For surface crystallization of tungsten carbide, this criterion suggests that transient effects can be neglected when annealing above 2600 K but become important at lower temperatures. The effects of nucleation transience on the isothermal kinetics of tungsten carbide crystallization were demonstrated by producing the isothermal transformation diagram (TTT curve) from cluster dynamics and steady-state models. In the diagram, the gradual deviation in the computed transformation time obtained from the two models becomes apparent at 2600 K and reaches more than an order of magnitude at the nose of the TTT curve (~2200 K).

Under dynamic conditions realized upon continuous cooling, transient effects attributed to the explicit dependence of the activation barriers on temperature may become significant when the barriers change faster than the rate at which nucleation relaxes. For surface crystallization of tungsten carbide, this criterion suggests that transient effects can be neglected for moderate-to-high cooling rates (10^4–10^6 K/s), while for ultrahigh cooling rates (10^8 K/s) transient effects may dynamically dominate the crystallization process. Consequently, the transient nucleation rate and crystallized fraction computed by means of cluster dynamics appear indistinguishable from their quasistatic counterparts for processing rates of 10^4 and 10^6 K/s, while for 10^8 K/s the results of the two models deviate substantially as the nucleation rate and crystallized fraction are overestimated by at least an order of magnitude at every undercooling temperature.

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