

Temperature Dependence of the Kinetics Rate of the Melting and Crystallization of Aluminum

V. I. Mazhukin^{a,b}, A. V. Shapranov^{a,b}, M. M. Demin^a, and N. A. Kozlovskaya^c

^a *Keldysh Institute of Applied Mathematics, Russian Academy of Sciences, Miusskaya pl. 4, Moscow, 125047 Russia; e-mail: vim@modhef.ru*

^b *National Research Nuclear University “MEPhI”, Kashirskoe sh. 31, Moscow, 115409 Russia*

^c *Lebedev Physical Institute, Russian Academy of Sciences, Leninskii pr. 53, Moscow, 119991 Russia; e-mail: menkova@sci.lebedev.ru*
Received December 14, 2015

Abstract—Using the molecular dynamics method, heterogeneous melting–crystallization of aluminum is simulated under conditions when the phase front propagates over the overheated–overcooled phase. The dependence of the phase front velocity on the temperature deviation from the equilibrium melting temperature is determined. The dependence obtained from atomistic simulation is used as an approximating function to obtain the temperature dependence of the kinetic rate in the analytical form. The steady-state temperature dependence of the kinetic rate $v(T_{sl})$ for extreme values of aluminum overheating–overcooling is constructed for the first time.

DOI: 10.3103/S1068335616090050

Keywords: overheated/overcooled states, kinetic rate, atomistic simulation, melting–crystallization.

Solid melting and liquid solidification are widespread phenomena in nature. There are known two melting/crystallization mechanisms: the heterogeneous (also called the surface or frontal) and homogeneous (bulk) ones. In the former case, within classical thermodynamics [1], solid melting and liquid solidification are defined as phase transformations of the first kind, which occur at a certain temperature T_m corresponding to equal Gibbs free energies of solid and liquid states. Motion of a continuous medium with a strong discontinuity surface (phase interface) on which thermal and optical characteristics (the internal energy ε (enthalpy H), the specific heat capacity C_p and thermal conductivity λ coefficients, density ρ , and pressure p) abruptly change corresponds to heterogeneous melting/crystallization mechanisms. At the phase interface $\Gamma_{sl}(t)$, the notion of the front motion velocity and two temperatures – the equilibrium melting temperature T_m (phase state temperature) and the temperature at the mobile interface $T_{sl}(t)$ (phase transition temperature) – are introduced. The homogeneous melting mechanism is characterized by new phase (liquid) nucleation in a certain volume of an overheated crystal. Similarly, homogeneous solidification occurs in a certain volume of overcooled liquid. Metastable overheated and overcooled states are inherent to all melting and solidification mechanisms. Limits of solid overheating and liquid overcooling implemented at very high heating–cooling rates (e.g., heating using intense ultrashort laser pulses) relate to fundamental problems which are actively studied [2–5] along with their numerous applications [6]. Homogeneous phase transitions are not considered in this paper.

In heterogeneous phase transitions, the basic quantity describing the kinetics of crystallization and melting processes is the phase interface velocity $v_{sl} = v(T_{sl})$, which is a function of the temperature T_{sl} deviation from the equilibrium melting temperature T_m , $(\Delta T - T_{sl} - T_m)$. In most theoretical studies, the function $v(T_{sl})$ is determined using some generalizations of the Wilson–Frenkel theory [7, 8]. One of the best known models is based on the mechanism of diffusion limitation of the crystallization–melting front velocity [9]. The crystallization–melting front velocity with diffusion limitation is expressed by the equation

$$v(T_{sl}) = C \exp\left(-\frac{Q}{k_B T_{sl}}\right) \left[1 - \exp\left(-\frac{L_m}{k_B T_m} \frac{\Delta T}{T_{sl}}\right)\right], \quad (1)$$

where C is the fitting parameter, Q is the activation energy, k_B is the Boltzmann constant, $k_B T_{sl}$ is the average thermal energy for one atom, and L_m is the latent melting heat.

Equation (1) was used to study the silicon melting–crystallization kinetics in a relatively small vicinity of the temperature T_m [10, 11]. The results were compared with the results of molecular–dynamics simulation with the Stillinger–Weber interaction potential [12] and experimental data. The comparison showed acceptable agreement. For pure metals, the molecular–dynamics simulation of the crystallization kinetics [10] using the Lennard–Johnson interaction potential [13] showed that at strong overcooling where the diffusion coefficient D is very small, the new phase growth rate in monatomic metals appeared much higher than the phase interface velocity determined from Eq. (1). The authors came to the conclusion that solidification should be limited by the collision frequency of liquid phase atoms with crystal faces, rather than by diffusion. In this case, the diffusion term (exponent $(-Q/k_B T_{sl})$) is replaced by the expression for the average thermal velocity $v_T = \sqrt{3k_B T/m}$. The expression for the propagation velocity of the melt–solid phase interface takes the form

$$v(T_{sl}) = \frac{af}{\lambda} v_T \left[\exp\left(\frac{L_m}{k_B T_m} \frac{\Delta T}{T_{sl}}\right) - 1 \right] = C \left(\frac{3k_B}{m} T_{sl}\right)_{sl}^{1/2} \left[\exp\left(-\frac{L_m}{k_B T_m} \frac{\Delta T}{T_{sl}}\right) - 1 \right], \quad (2)$$

where the coefficient $C = af/\lambda$, m , is the atomic mass, a is the interatomic distance, $\lambda < a$ is the mean free path of an atom of liquid before the collision with crystal surface, and $f < 1$ is the efficiency factor (a constant close to unity) taking into account the fact that some collisions are inefficient for the crystallization process.

The dependence obtained (2) was used to study the sodium melting–crystallization kinetics [14] in the vicinity of T_m . The results were compared with the results of dynamic simulation with the Lennard–Johnson interaction potential and experimental data. With a proper choice of fitting coefficients, quite satisfactory agreement of results was obtained.

The indicated approaches to the determination of the melting and crystallization kinetics contain two main disadvantages: a narrow temperature range (vicinity of the equilibrium temperature T_m) of overheated and overcooled states, in which the adequacy of the results is guaranteed; the existence of poorly studied quantities whose effect is taken into account using fitting parameters whose selection method is unknown deep in the metastable region of overheated and overcooled states.

The objective of this study is the development of a simple method for constructing the steady-state temperature dependence of the kinetic rate of metal melting–crystallization processes in a wide range of overheating and overcooling with predetermined approximation coefficients. To this end, atomistic simulation of the aluminum melting–crystallization kinetics with interaction potentials of the embedded atom method (EAM) [15] followed by approximation of expression (2) is used.

The molecular–dynamics simulation (MDS) is based on the model representation of the multiatomic molecular system in which all atoms are presented by material points whose motion is described in the classical case by Newton equations. Each of N point particles has the mass, radius vector, and velocity $m_i, \vec{r}_i, \vec{v}_i$, $i = 1 \dots N$, respectively; the interaction via the forces $\vec{F}_i = -\frac{\partial U(\vec{r}_1 \dots \vec{r}_N)}{\partial \vec{r}_i}$, $U(\vec{r}_1 \dots \vec{r}_N)$ is the potential energy; the interaction with external fields via the force \vec{F}_i^{ext} .

The mathematical model consists of a system of $2N$ differential equations, their difference analogue (difference scheme), the interatomic interaction potential, and specifically determined initial and boundary conditions. From the numerical solution of the system of differential equations, the coordinates and velocities (\vec{r}_i, \vec{v}) of all N particles are determined at any time point.

As an object of the study, aluminum was chosen, which has an fcc lattice in the solid state. The molecular–dynamics simulation of the heterogeneous metal melting–crystallization was performed under conditions of phase front propagation over the overheated/overcooled phase.

The calculated parallelepiped-shaped region $5 \times 5 \times 41$ nm in size is filled with 57600 particles interacting via the EAM potential for aluminum [15]. In all three spatial directions, periodic boundary conditions are imposed on calculated region boundaries, which ensure the constancy of the number of particles. In the region of the inter-phase boundary, the particles form a complex structure containing two phases: the crystalline and liquid ones. At the initial stage, the liquid phase occupies $\sim 18\%$ of the calculated region volume for studying the crystallization process; the crystalline phase occupies $\sim 80\%$.

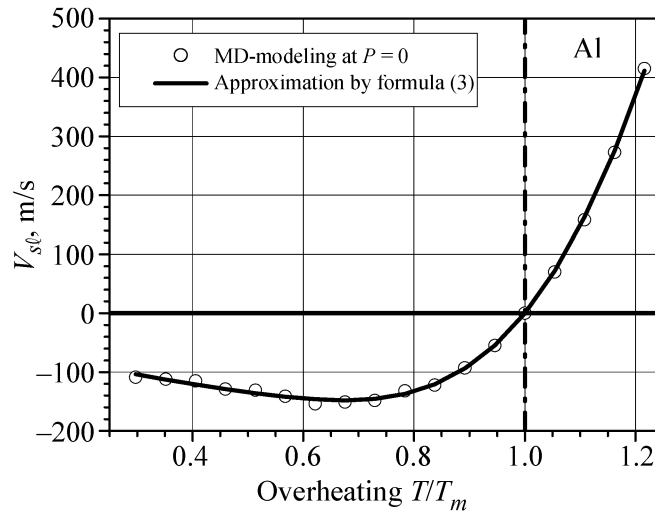


Fig. 1. Dependence of the melting/crystallization front velocity on the overheating/overcooling temperature for aluminum.

The melting–crystallization kinetics was studied by designing a series of numerical experiments in the range of liquid phase overcooling and solid phase overheating with respect to the equilibrium melting temperature T_m by -50% and $+20\%$, respectively.

The performed molecular–dynamics simulation resulted in the temperature dependence of the phase front velocity $v(T_{sl})$ in the range of limiting aluminum overheating and overcooling, denoted by circles in Fig. 1.

The following step was a comparison of the results of the molecular–dynamics simulation (MDS) with the results of the kinetic approach [10] (see Eq. (2)).

Table 1. Calculated (molecular–dynamics simulation) and experimental [17] values of T_m and L_m

Metal	Source	T_m , K	L_m , kJ/mol
Al	MDS	925	8.9
	[17]	933.2	10.8

Equation (2) contains two thermal parameters, i.e., the equilibrium melting temperature T_m and the latent melting heat L_m . Since these values in the molecular–dynamics approach can slightly differ from actual values (in view of imperfection of used interaction potentials), for adequate comparison of two curves, the same values of T_m and L_m as in the MDS should be used in Eq. (2). They were determined by the techniques described in [16] using MDS with the same potential [15]. The calculated results are listed in the table.

Using the temperature dependence $v(T_{sl})$ obtained by MDS as an approximating function, Eq. (2) was modified by introducing two additional coefficients α and β into the exponent and pre-exponential factor,

$$v(T_{sl}) = \beta \sqrt{\frac{3k_B}{m} T_{sl}} \left[\exp \left(\alpha \frac{L_m}{k_B T_m} \cdot \frac{T_{sl} - T_m}{T_{sl}} \right) - 1 \right]. \quad (3)$$

The best agreement with an error no more than a few percent in the whole temperature range was reached at the approximating coefficients $\alpha = 5.28$ and $\beta = 0.206$. Figure 1 shows the modified dependence (solid curve).

The obtained temperature dependence of the kinetic velocity $v(T_{sl})$ in the analytical form is important to formulate continual models describing rapid phase transitions in the approximation of various versions of the Stefan problem [18].

Thus, the simple method is proposed for constructing the most important kinetic characteristic of the heterogeneous metal melting–crystallization mechanism, i.e., the phase front velocity. The steady-state temperature dependence of the velocity $v(T_{s\ell})$ for limiting values of overheating–overcooling was constructed for the first time by the example of aluminum melting–crystallization. The constructed dependence contains two approximation coefficients independent of temperature. This method allows construction of the temperature dependences of the kinetic velocity $v(T_{s\ell})$ for a wide class of metals.

ACKNOWLEDGMENTS

This study was supported by the Russian Science Foundation project no. 15–11–00032.

REFERENCES

1. V. A. Kirillin, V. V. Sychev, and A. E. Sheindlin, *Technical Thermodynamics* (Energoatomizdat, Moscow, 1983) [in Russian].
2. B. Rethfeld, K. Sokolowski-Tinten, and D. von der Linde, *Phys. Rev.* **B65**, 092103 (2002).
3. B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. D. Miller, *Science* **302**, 1382 (2003).
4. A. Yu. Kuksin, G. E. Norman, V. V. Stegailov, and A. V. Yanilkin, *Comp. Phys. Com.* **177**, 34 (2007).
5. Y. Ashkenazy and R. S. Averback, *Acta Materialia* **58**, 524 (2010).
6. J. Cheng, C. Liu, S. Shang, et al., *Opt. Laser Technol.* **46**, 88 (2013).
7. H. A. Wilson, *Philos. Mag.* **50**, 238 (1900).
8. Ja. I. Frenkel, *Phys. Z. Sowjet Union* **1**, 498 (1932).
9. K. A. Jackson, *Interface Sci.* **10**, 159 (2002).
10. J. Q. Broughton, G. H. Gilmer, and K. A. Jackson, *Phys. Rev. Lett.* **49**, 1496 (1982).
11. M. D. Kluge and J. R. Ray, *Phys. Rev.* **B39**, 1738 (1989).
12. F. H. Stillinger and T. L. Weber, *Phys. Rev.* **B31**, 5262 (1985).
13. J. E. Jones, *Proc. R. Soc. Lond.* **A 106**(738), 463 (1924).
14. C. J. Tymczak and J. R. Ray, *Phys. Rev. Lett.* **64**, 1278 (1990).
15. V. V. Zhakhovskii, N. A. Inogamov, Yu. V. Petrov, et al., *Appl. Surf. Sci.* **255**, 9592 (2009).
16. V. I. Mazhukin, A. V. Shapranov, and V. E. Perezhigin, *Mathematica Montisnigri*, No. XXIV, 47 (2012).
17. *Physical Quantities. Handbook*, Ed. by I.S. GrigorTev and E. Z. Meilikhov (Energoatomizdat, Moscow, 1991), p. 288 [in Russian].
18. V. I. Mazhukin and A. A. Samarskii, *Surv. Mathem. Industry* **4**(2), 85 (1994).