

A NEW MODEL OF CRYSTAL GROWTH FROM UNDERCOOLED MELTS

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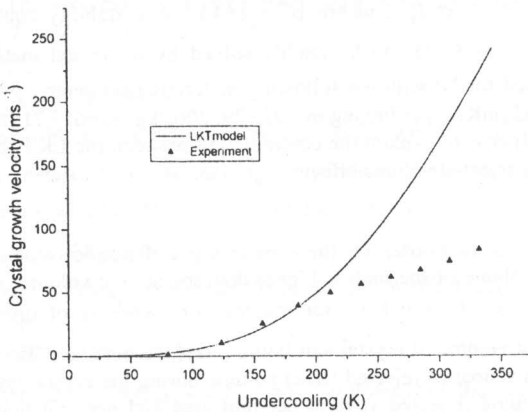
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Abstract. In spite of a number of attempts to improve the widely quoted model of Lipton, Travedi and Kurtz for crystal growth from undercooled melts, the agreement between the theory and the experiment, especially at high undercooling, is still poor. In the present study we show that the rejected volume at the crystal/liquid interface is the main reason for the contradictions. The interface of a growing crystal is a source of free-volume (an analog of vacancies in crystals) which has to diffuse towards the liquid. To transport the rejected volume from the crystal/liquid interface a driving force has to be created by cooling the liquid by some amount.

1. Introduction

In Fig.1 it is presented the crystal growth velocity as a function of undercooling temperature for crystal growth from undercooled liquid Ni. Symbols represent the experiment [1], the line - the

Fig.1. Crystal growth velocity as a function of undercooling



Lipton, Kurtz and Travedi (LKT) model [2]. At low undercoolings the agreement between the experiment and theory is very good but at high undercoolings it is very poor – the theory overestimates the crystal growth velocity considerably. Many attempts have been done to improve the agreement between the theory and experiment, unfortunately without essential progress up to now. For simplicity, further on we consider one-component systems, only.

In accordance with the LKT model there is relation between the total undercooling temperature, ΔT , growth velocity and curvature radius of the crystal [2]:

$$\Delta T = \Delta T_t + \Delta T_r + \Delta T_k, \quad (1)$$

where ΔT_t , ΔT_r and ΔT_k is thermal, curvature and kinetic undercooling term, respectively. Ivantsov [3] showed that because of the moving boundary condition the thermal undercooling is a

function of the velocity of crystal growth (i.e. the velocity of moving boundary) through the Peclet number:

$$\Delta T_i = \Theta_i I_v(P_i), \quad (2)$$

where $P_i = ur/2a$ is the thermal Peclet number, u the crystal growth velocity, r the crystal curvature at the considered point of the interface. $a = \kappa_l / c_p \rho$ is the heat diffusion coefficient in the liquid, where κ_l is the heat conductivity, ρ the density, c_p the specific heat capacity in the liquid phase. $\Theta_i = \Delta h_m / c_p$ is the limit for ΔT_i , Δh_m the heat of fusion, $I_v(x)$ is the Ivantsov function. The curvature undercooling

$$\Delta T_r = \Gamma K = 2\Gamma / r, \quad (3)$$

and the kinetic one

$$\Delta T_k = u / K_0, \quad (4)$$

had been introduced by Temkin [4], where $K=2/r$ is the surface curvature, Γ the Gibbs-Thomson parameter, given by $\Gamma = \sigma v_c / \Delta s_m$, where σ is the interfacial tension, v_c the atomic volume, Δs_m the entropy of fusion, K_0 is so called kinetic undercooling parameter. For a given total undercooling, Eq.(1) consists of two unknowns u and r , and consequently one more equation is needed. It was obtained in the frame of the marginal stability theory, developed by Mullins and Sekerka [5] and further improved by Lipton, Kurtz and Trivedi [2]:

$$r^2 = -\Gamma / [\sigma^* (-\bar{\kappa}_s \xi_s G_s - \bar{\kappa}_l \xi_l G_l)], \quad (5)$$

where G_s is outgoing thermal gradient in the solid, G_l in the liquid, $\bar{\kappa}_l = \kappa_l / (\kappa_l + \kappa_s)$ and $\bar{\kappa}_s = \kappa_s / (\kappa_l + \kappa_s)$ are the relative thermal conductivity in the liquid and the solid states, $\xi_l = 1 - 1 / \sqrt{1 + 1 / \sigma^* P_i^2}$, $\xi_s = 1 + 1 / \sqrt{1 + 1 / \sigma^* P_i^2}$, where $\sigma^* \approx 1 / 4\pi^2$ is a stability constant. G_s can be take zero and $G_l = \Theta_i P_i / r$. Eq.(1-2) can be readily solved by numerical methods.

The result, shown in Fig.1, is obtained for Ni with the following materials parameters: $\gamma=0.05$; $\sigma=0.250\text{J}/\text{m}^2$; $\kappa_l=75\text{J}/(\text{mKs})$; $\kappa_s=82.5\text{J}/(\text{mKs})$; $\rho_l=7905\text{kg}/\text{m}^3$; $H_f=292200\text{J}/\text{kg}$; $c_p=655.7\text{J}/(\text{Kkg})$; $T_m=1726\text{K}$. The aim of the present paper is to explain the contradiction between the LKT theory and the experiment by considering the rejected volume effect.

2. The rejected volume effect

The crystallization is a phase transition of first order, i.e. there are changes of atomic volume and atomic entropy. Usually the atomic volume of the melt is higher than the atomic volume of the crystal phase (with few exceptions). $\gamma = (v_l - v_c) / v_c$ for majority of metals is of order of $5 \cdot 10^{-2}$, where v_c and v_l is the atomic volume of crystal and liquid phase, respectively. Because of this the crystal/liquid interface is a source of rejected (free) volume during the crystal growth process. The flux of the rejected volume (rejected volume per unit area and per unit time) is $j = \gamma u$, where u is the crystal growth velocity at considered place of the interface. This flux creates a gradient of the free-volume in the vicinity of the interface

$$\nabla c = -\gamma / D_{fv} u, \quad (6)$$

where D_{fv} is the rejected volume diffusion coefficient, $c = \Delta v_l / v_l$ the rejected volume "concentration", Δv_l the rejected atomic volume. As a result a free-volume diffusion process accompanies any crystal growth process. The free-volume distribution obeys the usual Fick's diffusion law

$$\partial c / \partial t = D_{fv} \nabla^2 c, \quad (7)$$

with boundary conditions Eq.(6) and $c(\infty) = 0$, where $c(\infty)$ is the free-volume concentration far way from the interface. So formulated, Eq.(7) is mathematically equivalent to the Ivantsov heat diffusion equation [3] with the same solution:

$$c_i = \gamma'_v(P_v), \quad (8)$$

where c_i is the rejected volume concentration in the vicinity of interface, $P_v = ur/2D_v$ is the free-volume Peclet number, an analog to the thermal one. To transport the rejected volume throughout the liquid, a driving force should be created by an additional undercooling of the liquid, which we called "rejected volume undercooling" and denoted as ΔT_v . It can be found from the general expression for the crystal growth velocity, obtained by Dimitrov et al.[6]:

$$u = \Delta g_{lc} / \eta \delta^2 \quad (9)$$

where η is the viscosity, δ the nearest atomic distance. Δg_{lc} is the driving force of the crystal growth and equal to the local difference of the free energies of the liquid and crystal phases, taken per atom. Recently Dimitrov et al.[7] obtained for Δg_{lc} in the vicinity of the interface the following expression:

$$\Delta g_{lc} = \Delta g_{lc}^0 - 2\sigma v / r - k_B T c_i \Omega \quad (10)$$

where Δg_{lc}^0 refers to bulk phases, $\Omega = \alpha_l v_l / \kappa_T k_B$ is a dimensionless, characterizing the bulk liquid phase, thermodynamic quantity determined by the volume expansion coefficient, α_l , the isothermal compressibility coefficient, κ_T , and the atomic volume v_l . k_B is the Boltzmann's constant. The hard-sphere model of liquid metals and analysis of the experimental data give for Ω a value or order of 13. Taking into account the approximation $\Delta g_{lc}^0 = \Delta s_m (T_m - T_i)$ made by J.J.Thomson many years ago, from Eq.(9) and (10) we obtain

$$T_m - T_i = \Delta T_v + \Delta T_r + \Delta T_k, \quad (11)$$

with

$$\Delta T_v = \Theta_v I_v(P_v), \quad (12)$$

where $\Theta_v = \gamma(\alpha_l v_l / \Delta s_m \kappa_T) T_m$ is the free-volume undercooling limit, $\Theta_v \approx 0.5 T_m$ for most of the metals; T_m is the melting temperature, T_i the temperature at the interface. ΔT_r coincides exactly with Eq.(3) and ΔT_k with Eq.(4) if take

$$K_0 = \Delta s_m / \eta \delta^2. \quad (13)$$

where Taking into account the rejected heat effect, $\Delta T = T_m - T_i + \Delta T_i$, we generalized the LKT theory:

$$\Delta T = \Delta T_{LKT} + \Delta T_v \quad (14)$$

where $\Delta T_{LKT} = (\Delta T_i + \Delta T_r + \Delta T_k)$ follows from the LKT theory, with K_0 however determine by Eq.(13). If D_v were a known function of temperature, then the contribution of the rejected volume could be easily calculated. However the diffusion of the rejected volume is introduced for the first time in the present paper and indeed the mechanism of its diffusion is not known yet. Probably D_v is connected with the self-diffusion coefficient in the same way as the vacancy diffusion coefficient is connected with the self-diffusion coefficient in the crystals.

In the present paper we calculate $\Delta T_v = \Delta T - \Delta T_{LKT}$, where $(\Delta T, u)$ is an experimental point from the growth velocity as a function of total undercooling, and having obtained ΔT_v , then it is quite easy to calculate D_v . Depending on the undercooling it takes values from $10^{-2} m^2/s$ (at low undercoolings) to $10^{-12} m^2/s$ (at deep undercoolings), i.e. at low undercooling the free-volume diffusion coefficient is much more higher than the heat one (here

$a = \kappa_l / c_p \rho = 1.45 \cdot 10^{-5} \text{ m}^2 / \text{s}$), however at high undercooling the situation is totally opposite. Because of this transport of the rejected volume at the interface becomes the basic limiting factor for the crystal growth process.

3. Conclusions

The free-volume diffusion coefficient is approximately connected with the self-diffusion one as $D_{fv} = 10^7 D_s$. Then by analogy with the vacancy diffusion in the crystals $c_{fv} = 10^{-7}$ can be considered as the "equilibrium" concentration of the free-volume, corresponding to inherent fluctuation of the atomic volume in liquids. This means that density fluctuations are equalized over the system by diffusion process, like to the vacancy redistribution (diffusion) in crystals. At low temperatures the process is significantly slowed, volume fluctuation (or free-volume) can be trapped. Trapping of the rejected volume can lead not only to slowing the crystal growth but even to stop it, i.e. it can be the reason the crystallization to turn into glass transformation.

References

- [1]. R. Willnecker, D. Herlach, and B. Feuerbacher, *Phys. Rev. Lett.*, **62**, 2707 (1989).
- [2]. J. Lipton, W. Kurtz and Trivedi, *Acta Metall.* **35**, 957 (1987)
- [3]. G.P. Ivantsov, *Dokl. Akad. Nauk SSSR*, **58**, 567 (1947).
- [4]. D.E. Temkin, *Dokl. Akad. Nauk SSSR*, **132**, 1307 (1960).
- [5]. W.W. Mullins and R.F. Sekerka, *J. Appl. Phys.* **33**, 444 (1964).
- [6]. V.I. Dimitrov, A. Gungor, M. Kumru, A. Avinc, *A New Kinetic Equation for Phase Transformation of First Order*, Forth General Conference of the Balkan Physical Union, Veliko Tatnovo, 22-27 August 2000.
- [7]. V.I. Dimitrov, A. Gungor, M. Kumru, A. Avinc, *A Thermodynamic Theory of Crystal Growth from Undercooled Melts* (submitted for publication, April, 2000)

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