

Dependence of period of macrostructures on kinetic parameters under directed crystallization

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Abstract

In our previous works [Computat. Mater. Sci. 17 (2000) 555–559; Lett. Appl. Phys. 27 (11) (2001) 86–91], we have obtained an expression for a periodic distribution component under directed crystallization of eutectic alloys. This expression coincides with the experimental dependences obtained by Minford et al. [J. Am. Ceram. Soc. (1979) 154–162]. It was obtained from a model of directed crystallization which includes equations of heat conduction and diffusion. The model of directed crystallization contains in the common form a kinetic boundary condition. Dispersion equation of this problem contains a kinetic factor that is a derivative of the interface velocity with respect to temperature. This factor is contained in the expression of period dependence of eutectic pattern on interface velocity. But the dependence of interface velocity on temperature is related to kinetics of molecules addition of material to interface. Using the works by Cahn et al. [Acta Metall. 12 (1964) 1421, 8 (1960) 554], we found the dependence of the kinetic factor on parameters of kinetic theory of crystallization. In consequence, we have obtained dependences between parameters of a kinetic problem, i.e. problem that describes process of crystallization on microscopic level, and the problem of macrostructure formation. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The past several decades, directed crystallization has been extensively investigated to improve the microstructure of materials. But materials microstructure formation is a complex problem and at present we cannot give answers to all questions about phenomena of its formation. On one hand, multiformity of these structures means a complicated character of interaction of the various physical phenomena during their formation. On the other hand, reproducibility of outcomes of

practical derivation of the necessary structures means that their parameters are rigidly connected to conditions of crystallization. Formation of these structures is a result of processes of two various physical scales: molecules addition kinetics to interface and thermal-diffusion process. It is the cause of theoretical explanation complexity of the formation of these structures. The addition of molecules to the growing surface happens on a microscale. It can happen in different mechanisms of growth [6]. Mechanism of growth is theoretically, dependence of velocity V of the moving interface on kinetic supercooling ΔT_k

$$V = V(\Delta T_k), \quad (1)$$

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$$\Delta T_k = T_c - T(0). \quad (2)$$

Here, T_c is the solid–liquid transition temperature and $T(0)$ is the temperature of the interface.

The outcome of the thermal-diffusion process is the instability of the interface. The periodic structure arising is a result of this instability. After the classical work by Mullais and Sekerka [7], now there are many theoretical calculations [8], which give the qualitative correspondences of various mathematical models to experiments. However, now there are not enough papers which give convincing evidence of theoretical calculations to experiments. One such outcome is obtained in [1,2]. It is dependence of period of the eutectic pattern on the stationary interface velocity $\lambda(V_S)$. The set of equations considered contains heat conduction equations and diffusion equations. The model of this work contains, in a general view, a kinetic condition which is a model of the growth mechanism. In work [9] it is shown that this boundary condition determines a kind of dependence of period of the eutectic pattern on the interface velocity. The expression of period of the eutectic pattern was found from the dispersion equation of the system as

$$\lambda = \frac{\pi(\chi' + \chi)}{\varepsilon|\theta|}, \quad (3)$$

where χ and χ' are the thermal conduction factors for the liquid phase and solid phase accordingly, ε is the heat of solid–liquid transition, and θ is the kinetic factor that depends on the model of the growth mechanism. Essentially, that phase transition is a solid–liquid transition. If ε tends to zero, expression (3) gives the homogeneous distribution of the component concentration. The kinetic factor here is

$$\theta = - \left. \frac{\partial V}{\partial \Delta T_k} \right|_{\substack{T=T_S(0) \\ C=C_S(0)}}. \quad (4)$$

It has appeared in an outcome of the linearization of the boundary condition (1). In that specific case of growth by means of screw dislocations,

$$V = h_d \Delta T_k^2, \quad (5)$$

the dependence (3) has the form [1,2,9]

$$\lambda = \lambda_d = \frac{\pi(\chi' + \chi)}{\varepsilon\sqrt{h_d}V_S}. \quad (6)$$

This dependence coincides with the experiments. Therefore, formation of the periodic structure of components distribution in the solid phase depends both on processes which are described by the equations of the kinetics of molecules addition to the growing surface, i.e. processes happening on a microscale, and on processes which are described by equation of continuities, i.e. by heat conduction and diffusion equations. The mechanism of addition of molecules to the growing surface gives the kind of dependence of eutectic pattern period λ on the interface velocity V_S .

The processes of heat conduction and diffusion influence stability of the stationary regime of the interface movement and determine the period of instability modes. These outcomes allow us to consider the eutectic pattern as visualization of resonance properties of the complicated distributed parameter system. The interaction of the kinetic processes of the molecules association to the growing surface, processes of heat conduction and diffusion, happens in this system.

Our work has two purposes. In the first part, we show that the system gives the dependence $\lambda(V_S)$ which differs from the ones found in the works [1,2,9], but which also precisely coincides with the experimental dependences. We want to show that the kind of analytical dependence $\lambda(V_S)$ found in [1,2,9] is not casual concurrence, and the model gives correct dependences $\lambda(V_S)$ for eutectic crystallization of other composition.

Then we study the connection kinetics of molecules addition to the growing surface with formation of eutectic pattern in the case of growth by means of screw dislocations. We show that in the case of complete melt lamination, as it occurs under eutectic crystallization, the parameters of the model of growth mechanism are identically defined for each phase separately. We also show that the obtained analytical and experimental dependences allow us to find one kinetic parameter of a phase, i.e. one arbitrary kinetic parameter of molecules of each phase, if other parameters are known. We obtained the average of molecular layers involved in the crystallization. In the final

part, we demonstrate one formal outcome. We show that if the number of layers involved in crystallization varies by unity, then the eutectic pattern period varies by one order.

2. Connection of solutions of the continuity equations with the growth mechanism

The work [3] contains experimental dependences $\lambda(V_S)$ for eutectics of various compositions. Expression (6) precisely coincides with some of these dependences. Let us consider the kinetic coefficient h_d using both the experimental dependence $\lambda_{\text{exper}}(V_S)$ and the theoretical dependence (6). In this case, we shall obtain one value h_d for the considered material from the equation $\lambda = \lambda_{\text{exper}}$. However, theory of the growth mechanism by means of screw dislocations [4,5] gives for h_d , composite expression, which contains kinetic parameters for each kind of molecules. It is obvious that generally these parameters give different values of kinetic coefficient h_d for molecules of each phase of the eutectic melt. We have obtained this inconsistency because the solved problem contains constant values of the physical parameters, while the eutectic pattern results from the complete lamination of the melt.

If we used dependences of physical properties on concentration in the problem setting, we would obtain for each single-phase area of interface, values $\lambda_1, \lambda'_1, \varepsilon_1$ for one phase and $\lambda_2, \lambda'_2, \varepsilon_2$ for another phase of the eutectic pattern. Then (6) gives different values of kinetic coefficient h_{d1} and h_{d2} for each phase. We use this circumstance, that the dependence (6) precisely coincides with the experimental one, and we guess that the expression

$$\lambda_d = \frac{\pi(\chi'_i + \chi_i)}{\varepsilon_i \sqrt{h_{di} V_S}} \quad (7)$$

is also correct in the case when physical coefficients are different in each phase. Here $i = 1, 2$. In this work, we use these expressions for calculation of kinetic parameters of each separate phase.

From the dispersion equation, we have obtained expression for period of eutectic pattern (3), Eq. (6) [1,2]. Eq. (6) gives the dependence 1–5 in Fig. 1.

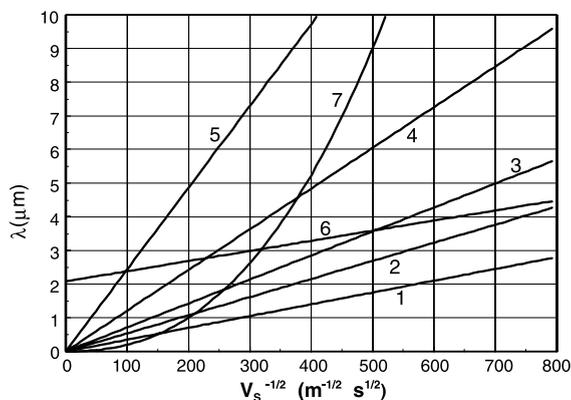


Fig. 1. Dependence of eutectic pattern on interface velocity.

The dependences in Fig. 1 correspond to the experimental dependences of the period pattern on the interface velocity [3]. The first kind of dependences are lines which intersect the ordinate axis at zero point; this kind of dependence is described by Eq. (6). This dependence in work [3] corresponds to melts crystallization: (1) $\text{Al}_2\text{O}_3\text{--ZrO}_2$, (2) Pb--Sn , (3) $\text{ZrO}_2\text{--MgO}$, (4) $\text{MgO--MgAl}_2\text{O}_4$ and (5) $\text{ZrO}_2\text{--Y}_2\text{O}_3$. The second kind is line intersecting the ordinate axis at a point different from zero. It corresponds to plot 6 (CaO--NiO). The third kind is curvilinear dependence. It corresponds to plot 7 ($\text{Zn}_5\text{B}_4\text{O}_{11}\text{--ZnB}_2\text{O}_4$). We had obtained analytic expression for dependences 1–5 [1,2]. Now we explain how we can obtain the dependences 6 and 7. The initial system [1,2,9] does not take into account surface tension. If we take into account the surface tension in the boundary condition, then in the case of growth by means of screw dislocations (5), we obtain for dependence of period of the eutectic pattern the expression

$$\lambda_d = \frac{\pi(\chi' + \chi)}{\varepsilon \sqrt{h_d V_S}} + \frac{2\pi(\chi' + \chi)\Gamma_n}{\varepsilon} \quad (8)$$

Γ_n is the normalized factor of surface tension. If the factor of surface tension is rather small, we obtain the former expression, which corresponds to lines 1–5. We obtain line 6 if the surface tension has a rather large value. If we take the model of exponential growth [6],

$$V_S = h_1 \exp\left(-\frac{h_2}{\Delta T_k}\right) \quad (9)$$

Here, h_1 and h_2 are constant factors and we obtain for the period of eutectic pattern the expression

$$\lambda_e = \frac{2\pi(\chi' + \chi)h_2}{\varepsilon V_S \ln(V_S/h_1)^2} + \frac{2\pi(\chi' + \chi)\Gamma_n}{\varepsilon}. \quad (10)$$

This expression gives plot 7 in Fig. 1. The calculated plots in Fig. 1 accurate to construction coincide with the experimental dependence of the work [3]. We took the values of parameters, during calculation, from the literature; the kinetic factor was obtained from the experimental dependence in the work [3].

3. The dependence of period eutectic pattern on the kinetic parameters of crystallization

According to the work [4], the dependence of the interface velocity on the kinetic supercooling for the model of growth by means of screw dislocations has the form

$$V = \frac{\beta(1 + 2g^{1/2})}{g} \frac{D_L L^2 (\Delta T_k^2)}{4\pi R T^3 \sigma V_m}. \quad (11)$$

Eqs. (5) and (2) give for kinetic factor h_d , the expression

$$h_d = \frac{\beta(1 + 2g^{1/2})}{g} \frac{D_L L^2}{4\pi R T^3 \sigma V_m}, \quad (12)$$

where D_L is the diffusivity in the liquid, R is the universal gas constant, σ is the surface tension, V_m

is the molar volume, L is the molar heat melting, T_c is the temperature of equilibrium phase transition, g is the diffuseness factor and β is the correction factor—this factor takes into account that jump length of molecules from liquid in solid phase differs from period of the crystalline lattice and takes into account symmetry of molecules. Parameter β is evaluated to equal about 10 for symmetric molecules [4].

According to the Khan theory [5], the factor g describes the diffuseness (diffuse) interface; g depends on number n of molecular layers in the area where the liquid phase passes in solid at the melting temperature. For a flat interface, g equals 1. For diffuseness interface, g has the form [10]

$$g = 2\pi^4 n^3 e^{-\pi^2 n/2}. \quad (13)$$

Eqs. (7) and (12) give relation between period of the eutectic pattern and parameter kinetic crystallization for the model of growth by means of screw dislocations.

Let us consider the experimental data of dependence of period of the eutectic pattern on the interface velocity in the work [3], which was described by Eq. (7) and correspond to lines 1–5 in Fig. 1. We use values of physical parameters for concrete materials to find kinetic factor h_d from Eq. (7). Values of h_d for different phases are shown in Table 1. On the other hand, the kinetic Khan theory gives for kinetic factor h_d Eq. (12). Therefore, we can find the value of any parameter in these expressions if we know the other parameters.

Table 1
The calculated and the experimental ‘*’ values of parameters

	h_d (m s ⁻¹ K ⁻²)	g	n	V^* (mkm s ⁻¹)	ΔT_k (K)
ZrO ₂	0.0228	1.6×10^{-4}	3.62	6.25	0.0165
Y ₂ O ₃	0.0531	4.8×10^{-5}	3.91		0.0108
MgAl ₂ O ₄	2.84	2.9×10^{-6}	4.58	2.77	0.000989
MgO	1.08	1×10^{-5}	4.3		0.0016
ZrO ₂	0.281	5.14×10^{-5}	3.9	1.56	0.002
MgO	3.28	7.1×10^{-6}	4.37		0.000699
Pb	23,500	6.3×10^{-9}	5.99	1.56	0.81×10^{-5}
Sn	9930	2.27×10^{-8}	5.7		1.2×10^{-5}
Al ₂ O ₃	17.4	6×10^{-7}	4.95	1.56	0.00031
ZrO ₂	1.35	5.1×10^{-6}	4.45		0.00107

Let the diffuseness parameter be unknown. Then, Eq. (12) gives for g a small expression

$$g \approx \frac{\beta}{h_d} \frac{D_L L^2}{4\pi R T_M^3 \sigma V_m} \quad (14)$$

Now we can calculate to what extent the atomic layers n is involved in the crystallization process for concrete materials using Eqs. (13) and (14). The calculated diffuseness factor and the number of atomic layers of the interface are given Table 1.

Since we know h_d , we can unambiguously define the kinetic supercooling from Eq. (5). We give the ΔT_k value in Table 1. Here also we give experimental values of interface velocity [3], which were used for calculation of ΔT_k . Like h_d , kinetic supercooling also has different values for each phase.

Fig. 2 shows the graph of dependence of diffuseness factor on the number of layers of the interface (Eq. (13)). We mark the calculated average value of diffuseness factor for concrete alloys. Generally, the disorder of the values n for any alloy is disposed in the range of one layer.

Now, we have the following question: How strongly crystallization kinetics influences period of the eutectic pattern? To answer this question, we used Eqs. (12) and (13) and we calculate the value of the period of eutectic pattern for different values of n . We changed the number of atomic

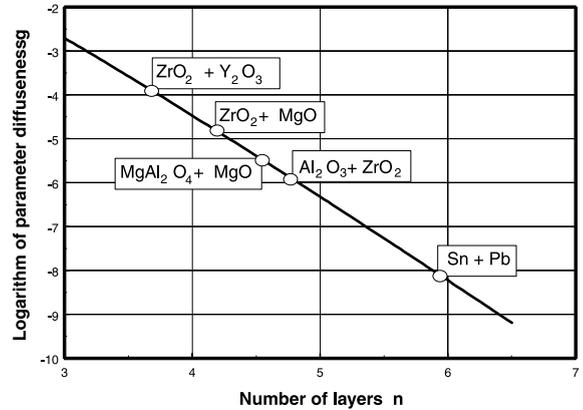


Fig. 2. Dependence of diffuseness factor on the number of layers of the interface.

layers involved in the process of crystallization, but we did not change the other parameters of the system. Fig. 3 demonstrates the dependences of the value of period of eutectic pattern on the velocity of crystallization at constant values of the number of atomic layers.

This dependence shows that if we magnify the number of molecular layers per unit, then the period of eutectic pattern is changed one order of magnitude. It is a formalistic result. But it demonstrates as far as strongly that both crystallization

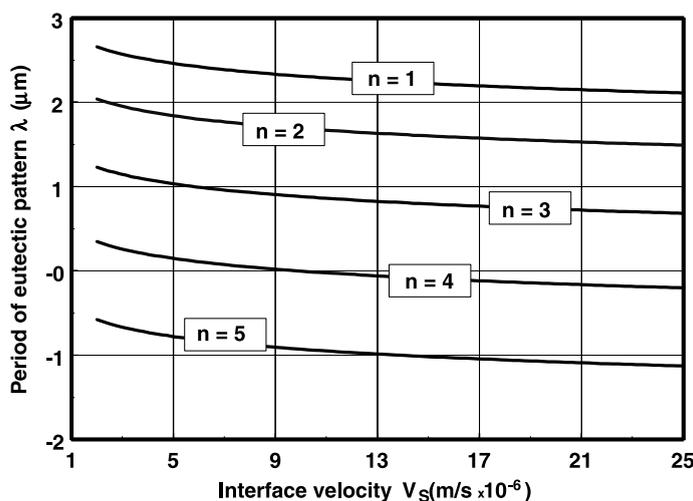


Fig. 3. Dependence of the value of period of eutectic pattern on the velocity of crystallization for different values of the number of atomic layers.

kinetics and macrostructure of component distribution are connected in nature. Now we cannot explain the physical sense of this result. May be it is connected with melt lamination. As an outcome of these calculations, we conclude that the eutectic solidification is a resonance system in which period of the eutectic pattern is the result of interaction of thermal, diffusion and kinetic parameters of the system. In experiments, the period depends only on interface velocity. The considered model of crystal growth gives this kind of dependence.

4. Conclusions

(1) Solid–liquid transition of the first order is essential that it was formed eutectic pattern. If the heat of solid–liquid transition tends to zero, the theory gives homogeneous distribution of components in crystal.

(2) The different kinds of experimental dependence of period of the eutectic pattern on the interface velocity can be explained by different models of crystallization kinetics.

(3) The value of kinetic supercooling for concrete material is unambiguously defined, if the dependence of period of the eutectic pattern on the interface velocity is known.

(4) Values of kinetic factors, which are contained in kinetic models of crystallization are unambiguously determined by dependence of macrostructure period on interface velocity and have different values for each solid phase of the interface.

(5) The variation of the atomic layers average of diffuseness per unit leads to the variation of macrostructure period of one order of magnitude.

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