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Formation of natural composites from melts, calculations and control of parameters of aperiodic impurity profiles

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The method for purposefully creating aperiodic radial impurity structures and controlling the shape of their spatial profiles in dilute alloys is presented. That is derived based on an analytical approach supported by the results of numerical calculations.

Keywords: unsteady directional controlled solidification, mobile impurities, aperiodic impurity profiles.

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1. Introduction

It is well known that with significant deviations from equilibrium, metastable phases may appear, often with properties qualitatively different from those of known substances in equilibrium states. Purposeful creation of certain metastable states makes it possible to significantly expand the set of available useful properties of materials without resorting to changing their chemical composition. The latter circumstance is very significant, because in the presence of chemical reactions in many cases (and with the participation of gases — always) it is necessary to create special original techniques to ensure relaxation of large mechanical stresses (see, for example, [1,2]).

In addition to durability, the standard technological requirements for new metastable materials are a sufficient degree of their uniformity, as well as a sufficiently high rate of formation of metastable phases. At the same time, the specified shape and size of the initial product-output product are realized by choosing the geometry and configuration of the installation.

A very common technological technique that allows achieving the necessary uniformity of materials obtained from melts and solutions is the method of directional crystallization. In this case, a temperature gradient is created, and the isotherm corresponding to the phase transformation (PT) temperature moves at a given speed. With a correctly chosen gradient sign and its sufficiently large value, nucleation in the volume of the material is suppressed, so that the morphology of the PT is as simple as possible, and the calculation of its kinetics is reduced to the calculation of the dynamics of an isolated phase front. In turn, the most frequently used in practice is the steady-state growth mode, in which it is sufficient to calculate the value of the constant velocity of the front under experimentally specified conditions.

However, this mode, as well as the generally accepted desire to obtain homogeneous materials-products, does not fully use the possibilities of creating metastable materials with the widest possible controlled set of properties. The latter, as is known, can critically depend on the structures created in the material, the scales of which can vary from macroscopic to nano.

Therefore, the strategy of manufacturing homogeneous products is not always the optimal choice. In many cases, the requirement of uniformity of the state of the material is dictated simply by the lack of a reliable technological technique for creating reproducible heterogeneous stable structures, as well as the lack of development of a theory that is convenient enough for practical calculations.

At the same time, experimental observations indicate that there are mechanisms in nature that lead to the appearance of such structures. In particular, numerous examples of such structures are known in mineralogy (see, for example, reviews of [3,4]). In minerals, the presence of structures often manifests itself in the form of multi-colored patterns having both complex and simple regular compositions. As an illustration, we present a photo of a mineral malachite sample, on the polished section of which the regular structure of rings colored with different intensities is visible, see Fig. 1. Although there is no detailed description of the hydrothermal processes responsible for the emergence of such a structure, its simplicity and unchanging nature, observed on a variety of samples from different deposits, suggest that the mechanism of their formation should be universal. Therefore, it can be hoped that to describe it, it is sufficient to use a simple model of the diffusion transport of impurities, the local change in the concentration of which provides a different intensity of coloring of the mineral.

The formation of structures with regular concentration ordering is also encountered in some metallurgical processes. Among them, processes with the formation of eutectic structures are especially important, since alloys possessing them have a number of useful properties [5]. As in the case of multicolored minerals, the mechanism of the appearance of regular eutectic grains is also based on the transport of impurity atoms [6].

Figure 1. Photo of a round layered structure of malachite.

In a series of our previous works, we proposed using stationary modes of fast directed crystallization [7–14] to create regular metastable composites. We have shown that under certain conditions, quite easily implemented in practice, the velocity of the melt (or solution) boundary — the crystal experiences self-oscillations around an experimentally set constant value of the velocity of the isotherm PT. It is important that it was possible to simplify the calculation of the dynamics of the interface with good accuracy to the solution of an ordinary differential equation for a nonlinear oscillator with negative friction. The parameters of the stable limit cycle of this equation determine not only the dynamics of the boundary, but also the oscillations of the impurity concentration on it. Since the diffusion coefficient of the impurity in the solid-phase material-product is small, the metastable periodic impurity profile arising in it is completely determined by these oscillations. Their characteristics can be purposefully controlled by changing the value of a given constant velocity of the isotherm V_{iso} and/or the magnitude of the external temperature gradient ∇T.

In this article, we will extend the methodology for creating flat periodic concentration structures in a situation where it is required to obtain simple regular, but not periodic, two-dimensional metastable concentration structures. It will be shown that for large radii of curvature, the calculation of aperiodic impurity profiles of materials-products can be simplified to solving the equation for a nonlinear oscillator with negative friction, which is under the action of an external force variable in time. Our numerical calculations have shown that it is easy to control the degree of aperiodicity of the emerging concentration structure, since the transition times from one quasi-periodic regime to another correspond to a small number of oscillation periods.

2. Description of the process and its physical model

Let us briefly recall the essence of the principle of directional crystallization, which underlies its several technological implementations, such as the methods of Bridgman, Chokhralsky, zone melting, fast directional crystallization, etc. The key point is the advance through the sample at a given speed of the isotherm corresponding to the temperature of the equilibrium PT of the melt−crystal. Behind this isotherm, its movement is tracked by a nonequilibrium interphase boundary, which tends to retain (less often — push out) impurities in the melt in front of it. Usually, a constant wiring speed V_{iso} is used to obtain a uniform distribution of impurities in the product material.

However, in a certain range of velocities V_{iso} and temperature gradients ∇T, the boundary retains the flat morphology of the isotherm surface, but its velocity $V(t)$ experiences periodic oscillations around a given constant velocity V_{iso} [7]. At minimum values of $V(t)$ the impurity concentration at the boundary approaches the equilibrium one, at maximum — it deviates noticeably from it. Thus, a long-lived metastable periodic profile of excess impurity concentration inherited from the melt is created in a cooled solid product, where the impurity diffusion is very slow.

For the first time, the theoretical possibility of the appearance of such periodic profiles was discovered in the works of Conti, who carried out numerical calculations within the framework of the phase field model for dilute alloys [15,16]. He noted that his numerical results differ markedly from the results of Kurtz and co-authors obtained within the framework of a purely phenomenological approach [17,18]. In the study [19], it was mathematically strictly shown how the phase field model used by Conti can be significantly simplified. The capillary-wave model derived in [19] was then used in [20–23] to perform an analytical calculation of the self-oscillatory dynamics of a plane interphase boundary during rapid directional crystallization of dilute alloys, as well as those formed in the solid phase at constant velocities V_{iso} of periodic impurity profiles.

In this paper, we use a generalization of the capillary-wave model to calculate the parameters of aperiodic impurity profiles arising in the mode of unsteady fast directional crystallization. For certainty, we will consider an experimental situation when a circular spot on the alloy surface is first melted by a laser beam, and then the irradiation power decreases, resulting in reverse recrystallization of the melt. It should be noted that in recent years there has been a significant increase in experimental capabilities for detailed observation of such processes *in situ*, with spatial and temporal nanorecision of the emerging metastable structures (see review [24]).

The equations of motion of the coordinate $R(t)$ of the melt−crystal boundary together with the diffusion equation for the local concentration $C(r, t)$ of the impurity entrained by the moving boundary take the form in this case

$$\frac{1}{p}\frac{\partial R}{\partial t} = -\frac{1}{R} + F_s - g\left(R - R_{\mathrm{iso}}(t)\right)$$

$$-\gamma \int_0^{+\infty} dr\, \frac{dC_{\mathrm{eq}}(r-R)}{dr}\left(C(r,t) - C_{\mathrm{eq}}(r - R(t))\right), \quad (1)$$

$$\frac{\partial C(r,t)}{\partial t} = \Delta_r\left[C(r,t) - C_{\mathrm{eq}}(r - R(t))\right], \quad (2)$$

where operator $\Delta_r = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)$, the initial position of the boundary is $R(t=0) = R_0 \gg 1$, a given time-dependent isotherm velocity $\dot{R}_{\mathrm{iso}}(t) = V_{\mathrm{iso}}(t)$, C_{eq} is the impurity profile corresponding to the equilibrium position of the boundary.

In (1), (2) a transition was made from the dimensional values of the problem, such as a given temperature gradient ∇T, a given rate of advance of isotherms $V_{\mathrm{iso}}(t)$, a given impurity concentration of the source material C_0, the profile of the equilibrium impurity concentration across the interface $C_{\mathrm{eq}}(r-R)$, the jump in impurity concentration at PT — ΔC_{eq}, latent heat of PT — L, temperature of PT — T_0, border width — δ, slope of the PT line on the phase diagram — $\frac{\partial T_0}{\partial C}$, the maximum velocity of the interphase boundary of pure matter — V_c, the rate of jump of an impurity atom into an adjacent cell — $V_d \approx D/\delta$, and D — coefficient diffusion to dimensionless variables

$$\frac{r}{\delta} \to r, \quad \frac{Dt}{\delta^2} \to t, \quad \frac{2(C - C_0)}{\Delta C_{\mathrm{eq}}} \to C, \quad (3)$$

and independent dimensionless parameters

$$\gamma = \left(\frac{\Delta C_{\mathrm{eq}}}{2}\right)^2 \frac{\rho\delta^3}{k_B T_0}, \quad \rho(T) = -\left(\frac{\partial T_0}{\partial C}\right)\frac{L}{T_0}\frac{1}{\Delta C(T)},$$

$$p = \frac{V_c}{V_d}, \quad F_s(R) = \frac{\delta^3 L}{k_B T_0}\left[\frac{T(R) - T_0}{T_0}\right],$$

$$g = \left(\frac{\delta^3 L}{k_B T_0}\right)\left(\frac{\delta \nabla T}{T_0}\right), \quad (4)$$

where k_B is the Boltzmann constant. To find solutions to the equations (1), (2), it is necessary to specify a specific type of functions $C_{\mathrm{eq}}(r-R)$ and $V_{\mathrm{iso}}(t)$. To simplify calculations, we will always choose the equilibrium impurity profile in the form of a smooth step: $C_{\mathrm{eq}}(x) = H(x)\exp(-x) + H(-x)[2 - \exp(x)]$, where $H(x)$ is the Heaviside function. System solutions (1), (2) for different modes of motion, the isotherms $V_{\mathrm{iso}}(t)$ will be obtained in the next section.

3. Dynamics of the melt–crystal interface and solid-phase impurity profiles at stationary and non-stationary isotherm velocities

For large radii of the melt spot $R(t)$, one can neglect can neglect the member $\frac{1}{r}\frac{\partial}{\partial r} \ll \frac{\partial^2}{\partial r^2}$ in (2); therefore, assuming the implementation of the relaxation mode of self-oscillations of the velocity of the interphase boundary, an approximate solution of the diffusion equation (2) can be obtained in exactly the same way as it was done in [8] for a flat boundary. Therefore, without repeating the derivation, we will only give the result for the value of the impurity concentration at the boundary

$$C(r=R,t) = C^{(1)}(R,t) + C^{(2)}(R,t), \quad (5)$$

$$C^{(1)}(r=R,t) = \int_{-\infty}^{R} dr' e^{-(R-r')} C'_{\mathrm{eq}}(r'), \quad (6)$$

$$C^{(2)}(r=R,t) = \frac{1}{2}\dot{v}\left(\frac{\partial^2}{\partial v^2}\right)\left(\frac{C^{(1)}(R,v) + C^{(1)}(R,0)}{v}\right). \quad (7)$$

After substituting the solution (5–7) into the equation (1) it turns into an equation for an oscillator having a non-linearly velocity-dependent friction force $G(v)$ and a mass $M(v)$:

$$M(\dot{R})\ddot{R} + G(\dot{R}) + g\left(R - R_{\mathrm{iso}}(t)\right) - F_s + \frac{1}{R} = 0, \quad (8)$$

where

$$G(v) := \frac{v}{p} - f(v) + f(0), \quad (9)$$

$$M(v) := -\frac{1}{2}\frac{\partial^2}{\partial v^2}\left[\frac{f(v) - f(0)}{v}\right], \quad (10)$$

$$f(v) := -\gamma \int_{-\infty}^{+\infty} dr C'_{\mathrm{eq}}(r) C^{(1)}(r,v). \quad (11)$$

Obviously, in the simplest case $V_{\mathrm{iso}}(t) = V_s = \mathrm{const}$ the equation (8) is a generalized Rayleigh equation, which, in the presence of a falling branch $G'(v) < 0$ of the friction force, has a stable limit cycle with a period T_s. Accordingly, for large melt spot sizes $R(t) \gg V_s T_s := d$ a ring-shaped impurity profile with a spatial period of d will arise.

If the deviations of the isotherm velocity from its average value V_s are small, $V_{\mathrm{iso}}(t) = V_s + \varepsilon V(t)$, $\varepsilon \ll 1$ (this assumption guarantees that repeated melting of the crystallized areas of the material is impossible), then equation (8) can be rewritten as

$$M(\dot{R})\ddot{R} + G(\dot{R}) + g(R - V_s t) - F_s + \frac{1}{R} = g\left(R_{\mathrm{iso}}(t) - V_s t\right), \quad (12)$$

i.e. it takes the form of a generalized Rayleigh equation containing a time-dependent external force.

Equation (12) is useful in two ways. Firstly, the nature of its possible solutions has been studied mathematically well enough and their classification [25,26] has been constructed. Secondly, for specific experimental cases, it can be solved numerically much easier and faster than an integro-differential system of equations (1), (2). It is advisable to use both of these factors for a preliminary

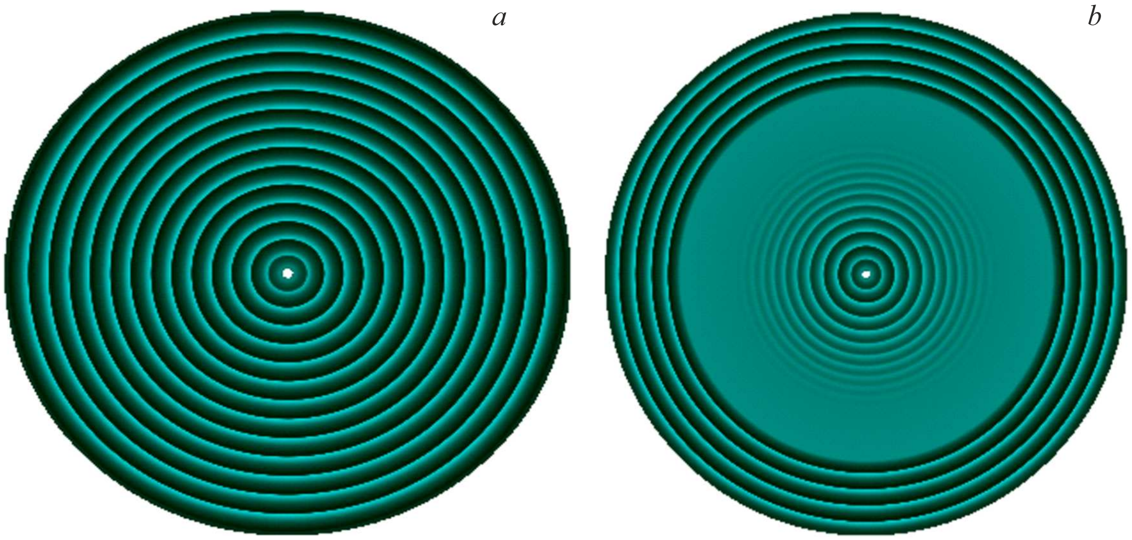

Figure 2. Impurity concentration distribution obtained by numerical solution of the system (1), (2): *a*) at a constant wiring speed $V_{\text{iso}}(t) = 0.4$; *b*) at speed $V_{\text{iso}}(t) = V_0 + kt \cdot [H(t) - H(t - \Delta t)]$ for parameter values $V_0 = 0.4$, $\Delta t = 2 \cdot 10^4$, $k = 10^{-5}$.

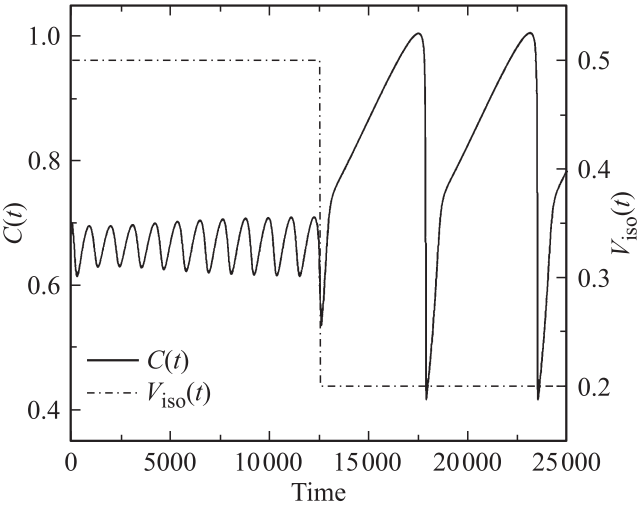

Figure 3. Impurity concentration distribution obtained by numerical solution of the system (1), (2) with „switching“ the speed $V_{\text{iso}}(t)$ according to (13), with parameter values $V_1 = 0.5$, $V_2 = 0.2$, $\Delta t = 1.25 \cdot 10^4$, $\tau = 50$.

search for the optimal choice of values of control parameters: functions $V_{\text{iso}}(t)$ and values ∇T.

The most interesting issue for applications is the possibility of creating and effectively managing a variety of profiles of impurity structures that occur in a solidified material. In particular, it is important how compactly the areas of rings of different radii can be arranged when „switching“ isotherm velocity from one value to another (see, for example, [27]). To find out, we performed a series of numerical calculations of the system of equations (1), (2) for different modes $V_{\text{iso}}(t)$. Some of the results obtained are shown in Figures 2 and 3.

The law of switching $V_{\text{iso}}(t)$ from V_1 to V_2 was chosen by us in Fig. 3 in the form

$$V_{\text{iso}}(t) = V_1 + \frac{V_2 - V_1}{2}\left(\text{th}\left(\frac{t - \Delta t}{\tau}\right) + 1\right), \qquad (13)$$

where τ — is the characteristic switching time.

From these figures we see that: a) it is not difficult to choose the mode $V_{\text{iso}}(t)$, which provides almost any given impurity profile in a solid material-product, and b) kthe transition areas from one characteristic profile shape to another are quite short and correspond, as a rule, to just a few concentration oscillations.

4. Conclusion

The article discusses the possibilities of using the method of fast unsteady directional crystallization to create metastable microstructures with a given radial profile of impurity concentration. It is shown that for the practical determination of the time dependence of the velocity of the isotherm of the phase transformation of the melt−crystal, which ensures the occurrence of such profiles, including aperiodic, with good accuracy, it is sufficient to obtain a solution of an ordinary nonlinear differential equation of the type of the generalized Rayleigh equation containing the contribution of a variable external force.

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Conflict of interest

The authors declare that they have no conflict of interest.

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